

THE JOURNAL OF THE IRON AND STEEL INSTITUTE

Vol. CLIV

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PREFACE.

THE present volume contains twenty-two papers—nine of which were issued under the auspices of the Joint Research Committees of this Institute and the British Iron and Steel Research Association, and one of which reported on an investigation carried out with the aid of a grant from the Andrew Carnegie Research Fund—that were presented at the Autumn Meeting of this Institute held in London on 13th and 14th November, 1946, together with any discussion and correspondence to which they gave rise, and the authors' replies; also the discussion, correspondence, and authors' replies on two papers published in the preceding volume of the *Journal* and on Special Report No. 37, "The Influence of Port Design on Open-Hearth Furnace Flames," by J. H. Chesters and M. W. Thring. The following Special Reports were included in the programme of the Autumn Meeting, and publication notices on them will be found in this volume:

Special Report No. 32: "Third Report on Refractory Materials." By the Joint Refractories Research Committee of the British Iron and Steel Research Association and the British Refractories Research Association.

Special Report No. 33: "The Development of Monolithic Dolomite Linings." By the Technical Panel of the Basic Furnace Linings Committee.

Special Report No. 34: "First Report of the Rolling-Mill Research Sub-Committee of the Iron and Steel Industrial Research Council."

Special Report No. 35: "Second Report on the Development of Monolithic Dolomite Linings." By the Technical Panel of the Basic Furnace Linings Committee.

Special Report No. 36: "Symposium on the Hardenability of Steel." Organized by the Technical Advisory Committee of the Special and Alloy Steels Committee (Ministry of Supply) and The Iron and Steel Institute.

Special Report No. 37: "The Influence of Port Design on Open-Hearth Furnace Flames." By J. H. Chesters and M. W. Thring.

The above-mentioned matter, together with the Minutes of Proceedings of the Meeting, and biographical notes on deceased Members, comprises Section I. of this *Journal*.

Section II. is devoted to a survey of the literature of the manufacture and properties of iron and steel and kindred subjects, and consists of a collection of abstracts of articles from the Transactions and Proceedings of scientific societies and from the technical press. This Section also contains reviews of recent books and bibliographies of literature dealing with the manufacture and properties of iron and steel. The matter included in this Section has already appeared in the *Bulletin of The Iron and Steel Institute*.

In front of the title-page are inserted lists of Bibliographies and Special Reports issued by the Institute, together with a list of Translations made available between 1st January, 1947, and 31st December, 1947.

4, GROSVENOR GARDENS,

LONDON, S.W. 1.

31st December, 1947.

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ABBREVIATIONS AND SYMBOLS.


Å.	Ångstrom unit(s) = 1×10^{-10} m.	kX.	crystal Ångstrom(s) = 1000 Siegbahn X-units.
A.C.	air-cooled; alternating current.	lb.	pound(s).
A.H.	air-hardened.	L.F.	low-frequency.
amp.	ampere(s).	M	molar (solution).
amp.hr.	ampere-hour(s).	m.	metre(s).
approx.	approximately.	m.amp.	milliampere(s).
at.-%	atomic per cent.	max.	maximum.
at.wt.	atomic weight.	mg.	milligramme(s).
atm.	atmosphere(s) (pressure).	min.	minimum; minute(s).
A.W.G.	American wire-gauge.	ml.	millilitre(s).
Bé.	Baumé (scale).	mm.	millimetre(s).
b.h.p.	brake horse-power.	m.m.f.	magnetomotive force.
B. & S.	Brown and Sharpe (gauge).	m.p.	melting point.
B.o.T.	Board of Trade.	mV	millivolt(s).
b.p.	boiling point.	mμ	millimicron = 1×10^{-9} m. = 10 Å.
B.T.U.	Board of Trade unit(s).	N.	normal (solution).
B.Th.U.	British thermal unit(s).	N.T.P.	normal temperature and pressure.
B.W.G.	Birmingham wire-gauge.	O.H.	open-hearth; oil-hardened.
C.	centigrade (scale).	O.Q.	oil-quenched.
cal.	calorie(s).	oz.	ounce(s).
c.c.	cubic centimetre(s).	p.d.	potential difference.
c.d.	current density.	pH	hydrogen-ion concentration.
c.g.s.	centimetre-gramme-second unit(s).	p.p.m.	parts per million.
cm.	centimetre(s).	r.p.m.	revolutions per minute.
coeff.	coefficient(s).	sec.	second(s).
conc.	concentrated.	sp.gr.	specific gravity.
const.	constant(s).	sq.	square.
cu.	cubic.	S.W.G.	standard wire-gauge.
cwt.	hundredweight(s).	T.	tempered.
D.C.	direct current.	temp.	temperature.
dia.	diameter.	V.	volt(s).
dil.	dilute.	VA.	volt-ampere(s).
dm.	decimetre(s).	W.	watt(s).
e.m.f.	electromotive force.	Wh.	watt-hour(s).
e.v.	electron volt(s).	W.G.	water-gauge.
F.	Fahrenheit (scale).	W.Q.	water-quenched.
ft.	foot, feet.	wt.	weight.
ft.lb.	foot-pound(s).	wt.-%	weight per cent.
g.	gramme(s).	yd.	yard(s).
gal.	gallon(s).	γ	microgramme(s) = 1×10^{-6} g.
H.F.	high-frequency.	μ	micron(s) = 1×10^{-6} m.
h.p.	horse-power.	μμ	1 millionth micron = 1×10^{-12} m. = 0.01 Å.
h.p.hr.	horse-power-hour(s).	Ω	ohm(s).
hr.	hour(s).	°	degree (arc or temperature).
in.	inch(es).	'	minute of arc; foot (feet).
in.lb.	inch-pound(s).	"	second of arc; inch(es).
I.S.W.G.	Imperial standard wire-gauge.	<	less than.
K.	absolute temperature (Kelvin scale).	>	greater than.
kg.	kilogramme(s).	≥	not less than.
kg.cal.	kilogramme-calorie(s).	≠	not greater than.
kg.m.	kilogramme-metre(s).	≤	equal to or less than.
km.	kilometre(s).	≥	equal to or greater than.
kV.	kilovolt(s).	≠	not equal to.
kVA.	kilovolt-ampere(s).	≡	identically equal to.
kW.	kilowatt(s).	≈	approximately equal to.
kWh.	kilowatt-hour(s).	∝	proportional to.

SECTION I.

*MINUTES OF PROCEEDINGS AND PAPERS OF
THE IRON AND STEEL INSTITUTE.*

AUTUMN MEETING

1946



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MINUTES OF PROCEEDINGS

AND

PAPERS AND DISCUSSIONS

AT THE

AUTUMN MEETING IN LONDON, 1946.

THE AUTUMN MEETING OF THE IRON AND STEEL INSTITUTE was held at The Institution of Civil Engineers, Great George Street, London, S.W.1, on Wednesday and Thursday, November 13 and 14, 1946, the PRESIDENT (Dr. C. H. Desch, F.R.S.) being in the Chair. The sessions on the Wednesday started at 10 A.M. and 2.30 P.M., and on the Thursday at 9.30 A.M. and 2.30 P.M., and there was a film display on the Wednesday from 8.0 P.M. to 9.30 P.M.

The Minutes of the previous Meeting held in London on May 1 and 2, 1946, were taken as read and signed.

WELCOME TO FOREIGN MEMBERS.

The PRESIDENT (Dr. C. H. Desch, F.R.S.): I wish to offer a welcome to our foreign visitors. It happens that on this occasion we have a number of them present. As I have not a complete list, I shall not mention them by name, but we have always been anxious to maintain the largely international character of this Institute, and we are glad to have visitors from the Continent. To one of them I shall have to make special reference in a few moments.

OBITUARY.

The PRESIDENT: I have to report the death of a prominent foreign Member of the Institute, Professor Léon Guillet, which took place on May 9, 1946. This is our first meeting since then. He was an Honorary Vice-President of the Institute and a Carnegie Gold Medallist. A good many members of the Institute who were in the habit of going to meetings in France will remember Professor Guillet, and he was very well known on account of his writings.

CHANGES ON THE COUNCIL.

The SECRETARY (Mr. K. Headlam-Morley) reported that at the meeting of the Council held the previous day Dr. Desch had been asked to accept nomination as President for a second year of office starting at the Annual Meeting in 1947, and had agreed to do so. He also announced that the Council had decided to nominate Mr. J. S. Hollings and Mr. Cyril Lloyd to be Honorary Vice-Presidents, in consideration of the lengthy and valuable service which they had given to the Institute. The following changes on the Council since the last meeting had also to be announced:

Vice-President.—Mr. James Mitchell.

Member of Council.—Mr. W. F. Cartwright.

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Dr. J. E. Hurst and Mr. W. W. Stevenson to be Honorary Members of Council, nominated by the Institution of Metallurgists.

Mr. Chris Moody to be an Honorary Member of Council, in succession to Mr. J. H. Patchett, during his period of office as President of the Cleveland Institution of Engineers.

Mr. G. J. Jones to be an Honorary Member of Council, in succession to Captain H. Leighton Davies, during his period of office as President of the Swansea and District Metallurgical Society.

Mr. G. B. Morrison to be an Honorary Member of Council, in succession to Dr. J. E. Hurst, during his period of office as President of the Staffordshire Iron and Steel Institute.

The following were due to retire at the next Annual General Meeting, and were eligible for re-election:

Vice-Presidents.—Captain H. Leighton Davies and Mr. G. H. Latham.

Members of Council.—Mr. H. H. Burton, Mr. D. F. Campbell, Mr. R. A. Hacking, and Mr. N. H. Rollason.

FORTHCOMING MEETINGS.

The SECRETARY announced that the Annual General Meeting, 1947, would be held from Wednesday to Friday, May 14 to 16. A discussion on the hardenability of steel, in the form of a symposium, would be held on Wednesday, May 14, and the Annual Dinner on Thursday, May 15.

SUMMER MEETING IN SWITZERLAND.

The PRESIDENT: In addition to the meetings just announced by the Secretary, I have to say that with the kind assistance of the Swiss steel

and engineering industries it has been arranged that a Summer Meeting will be held in Zürich from July 9 to 16, 1947, to be followed by tours lasting until July 19, on the lines of previous Autumn Meetings. The Secretary has been in Switzerland and has seen our friends there, and a most excellent programme has been drafted.

The Swiss steel industry, as we know, is not large in comparison with that of some other countries, but it is of an extremely interesting character, and there will be an opportunity there of seeing some works with very modern methods, and particularly some quite recent developments. We have with us to-day Dr. R. Durrer, the Managing Director of the von Roll Company, who has kindly agreed to be Chairman of the Reception Committee, and Dr. Meinrad Lienert, Managing Director of the Swiss Association for the Encouragement of Trade, will be the Honorary Secretary.

We hope before long to be able to announce the details of the programme, which I think will be a very interesting one. It will cover a number of works and institutes in Switzerland, together with a visit to one French works, Ugine, in Savoy, across the frontier. In connection with this we have to acknowledge the very great help given by Dr. Durrer, and I particularly welcome him on this occasion. We are glad that he has been able to attend this meeting.

OTHER INSTITUTE AFFAIRS.

The PRESIDENT: There are a few other matters relating to the Institute which I wish to mention:

Publications.—The monthly *Journal* of the Institute, the issue of which had been arranged in 1939, but which had to be postponed on the outbreak of war, will start publication next January. One copy of each monthly issue will be supplied to each member, and bound volumes will be on sale on preferential terms. The details will be announced shortly. The format has been altered to quarto size, and those who have already seen the specimen copies are very well satisfied with the type of publication. We believe that this will considerably increase the services which the Institute is able to offer.

Information Service.—With the co-operation of the British Iron and Steel Research Association, the Information Service, which has been operating in conjunction with our Joint Library with the Institute of Metals, is being extended, so that the facilities for obtaining information will be very considerably increased in future. The Research Association naturally expects to make a great deal of use of those facilities.

Iron and Steel Engineers Group.—The Iron and Steel Institute Engineers Group, the formation of which was announced at the Annual Meeting this year, has begun well. It operates within the framework of the Institute, and there are already very nearly a thousand members of that Group. The first meeting was a great success, with a good attendance and excellent discussions. The next meeting will be held on December 11, 1946, when the two subjects for discussion will be Lubrication in Iron and Steel Works and Roll-Neck Bearings. Great credit is due to Mr. Cartwright, the Chairman of the Group, and to the members of his Committee. It seems likely to be a very active body.

Powder Metallurgy Symposium.—At the request of a number of members, the Council has decided to organize a symposium of papers on Powder Metallurgy. That will be held in London on June 18 and 19, 1947. It is hoped that we shall then have the co-operation of the non-ferrous industries, because naturally powder metallurgy is not entirely confined to iron.

The formation of a Study Group on Powder Metallurgy is being considered, but nothing definite will be done until after the holding of the symposium.

Affiliation with Local Societies.—We have arrangements working now for affiliation with a number of local societies, and we hope that as conditions become more normal the value of these connections will increase.

Educational.—Under the auspices of the Joint Education Committee, a brochure* on metallurgy as a scientific career in industry has been issued and given a wide circulation amongst schools and education authorities, with the co-operation of the Ministry of Education.

A good start has been made with the scheme for National Certificates in Metallurgy. Four technical colleges held examinations at the end of the last school year, and over twenty courses have been approved for the present academic year. The Committee has decided to award prizes to a number of those who distinguish themselves in the examination.

BALLOT FOR THE ELECTION OF MEMBERS AND ASSOCIATES.

Mr. R. STEEL (Northallerton) and Mr. R. D. LANGRISH (Ewell, Surrey), who had been appointed scrutineers of the ballot for the election of Members and Associates, reported that the following two hundred and sixty-two candidates for membership and seventy-nine for associate-ship had been duly elected:

* Joint Committee on Metallurgical Education, "Metallurgy—A Scientific Career in Industry." London, 1946: The Fanfare Press.

MEMBERS.

- ADAMS, ORLANDO PERCIVAL, Pittsburgh, Pa., U.S.A.
 AGUIRRE, JOSÉ MARIA, Guipúzcoa, Spain.
 ANGELL, FRANK, A.M.I.E.E., A.M.I.Mech.E., East Moors, Cardiff.
 ARCHIBALD, WILLIAM ANDERSON, Ph.D., B.Sc., London.
 ARECHAVALA, MANUEL, Bilbao, Spain.
 BALAKRISHNAN, P. R., Bhadravati, India.
 BANNER, GEORGE JAMES, A.I.M., Wednesbury, Staffs.
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 BATES, FREDERICK JOHN, Birmingham.
 BELL, JAMES, Birmingham.
 BELLAMORE, DAVID H., New York City, U.S.A.
 BERRY, RICHARD WILLIAM, A.R.C.S., B.Sc., London.
 BJÖRKMAN, PER O., Västerås, Sweden.
 BLOOD, *Commander* MORICE, R.N. (Retd.), London.
 BOAG, DAVID JAMES WILSON, B.Sc.(Hons.), A.M.I.Mech.E., Croydon, Surrey.
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 BOSCH, M. F. M., Ghent, Belgium.
 BOTH, GERARDUS JAN JACOBUS, Utrecht, Holland.
 BOUVIER, LÉOPOLD, Luxembourg.
 BOWEN, HUBERT NORMAN, Port Talbot, Glam.
 BRADLEY, JOHN NEWSUM, B.Sc.(Hons.), A.R.S.M., A.R.I.C., Portsmouth.
 BRAMLEY, LIONEL NAPIER, Ph.D., M.Sc., D.I.C., London.
 BRANDES, ERIC ADOLPH, B.Sc., A.R.C.S., Chalfont St. Peter, Bucks.
 BRANDT, DAVID JULIUS OSCAR, B.Sc.(Eng.), London.
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PRESENTATION OF PAPERS.

A list of the papers and reports included in the programme of the Meeting will be found on p. 6 P. Those marked with an asterisk will be found in the No. I. volume of the *Journal* for 1946. The following were presented for verbal discussion :

Wednesday, November 13 :

- "The Influence of Port Design on Open-Hearth Furnace Flames." By J. H. CHESTERS and M. W. THRING. (Special Report No. 37.)
- "A Heat-Flow Meter for Use in Furnaces." By R. H. BAULK and M. W. THRING."

The above papers were discussed jointly.

*Thursday, November 14 :**Morning Session.*

- "The Origin and Constitution of Certain Non-Metallic Inclusions in Steel." By J. R. RAIT and H. W. PINDER.
- "The Neutralization of Sulphur in Cast Iron by Various Alloying Elements." By H. MORROGH.

The above papers were discussed jointly.

- "The Removal of Hydrogen from Steel." By J. H. ANDREW, H. LEE, A. K. MALLIK, and A. G. QUARRELL.

Afternoon Session.

- "The Formation of Anti-Corrosive Compositions for Ships' Bottoms and Underwater Service on Steel." By F. FANCUTT and J. C. HUDSON.
- "Report on Anti-Fouling Research, 1942-44." By J. E. HARRIS.
- "Interim Descriptive Statement on the Leaching-Rate Test for Ships' Anti-Fouling Compositions." By the JOINT TECHNICAL PANEL ON THE LEACHING-RATE TEST.

The above papers were discussed jointly.

- "New Annealing Plant for Steel Strip in Coils at the Whitehead Iron and Steel Co., Ltd., Newport, Mon." By B. JONES and I. JENKINS.

Complete List of Papers and Reports Presented at the Autumn Meeting in London, 1946.

- JOINT TECHNICAL PANEL ON THE LEACHING-RATE TEST: "Interim Descriptive Statement on the Leaching-Rate Test for Ships' Anti-Fouling Compositions." (Paper No. 19/1946 of the Corrosion Committee (submitted by the Marine Corrosion Sub-Committee).)
- PHYSICS DIVISION, NATIONAL PHYSICAL LABORATORY: "The Physical Properties of a Series of Steels.—II." (Paper No. 23/1946 of the Alloy Steels Research Committee (submitted by the Thermal Treatment Sub-Committee).)
- *J. H. ANDREW, H. LEE, A. K. MALLIK, and A. G. QUARRELL: "The Removal of Hydrogen from Steel." (Paper No. 22/1946 of the Alloy Steels Research Committee (submitted by the Hair-Line Crack Sub-Committee).)
- *K. BALAJIVA, A. G. QUARRELL, and P. VAJRAGUPTA: "A Laboratory Investigation of the Phosphorus Reaction in the Basic Steel-Making Process." (Paper No. 34/1946 of the Ingot Committee.)
- *R. H. BAULK and M. W. THRING: "A Heat-Flow Meter for Use in Furnaces."
- J. H. CHESTERS and M. W. THRING: "The Influence of Port Design on Open-Hearth Furnace Flames." (Special Report No. 37.)
- L. COOK: "The Melting Shop of the Turkish State Iron and Steel Works, Karabük."
- W. DAVIES: "The Fundamental Characteristics of Moulding Sands." (Paper No. 20/1946 of the Steel Castings Research Committee (submitted by Dr. W. J. REES, through the Moulding Materials Sub-Committee).)
- F. FANCUTT and J. C. HUDSON: "The Formulation of Anti-Corrosive Compositions for Ships' Bottoms and Underwater Service on Steel.—Part II." (Paper No. 18/1946 of the Corrosion Committee (submitted by the Marine Corrosion Sub-Committee).)
- J. E. HARRIS: "Report on Anti-Fouling Research, 1942–44." (Paper No. 20/1946 of the Corrosion Committee (submitted by the Marine Corrosion Sub-Committee).)
- J. C. HUDSON and T. A. BANFIELD: "The Protection of Iron and Steel by Metallic Coatings." (Paper No. 21/1946 of the Corrosion Committee (submitted by the Protective Coatings (Corrosion) Sub-Committee).)
- J. E. HURST and R. V. RILEY: "Routine Spectrographic Analysis of Cast Iron."
- I. JENKINS: "Gas-Carburizing."
- B. JONES and I. JENKINS: "New Annealing Plant for Steel Strip in Coils at the Whitehead Iron and Steel Co., Ltd., Newport, Mon."
- F. H. KEATING: "Experimental Work on the Production and Use of Radiographed Steel Castings for Service at High Pressures."
- I. M. MACKENZIE: "The Rapid Determination of Reactive Oxygen in Open-Hearth Steel." (Paper No. 36/1946 of the Ingot Committee (submitted by the Sub-Committee on Gaseous and Non-Metallic Inclusions in Steel).)
- D. MANTERFIELD and J. R. THURSTON: "Improvement in Design of Immersion Pyrometers for Liquid Steel Temperatures." (Paper No. 35/1946 of the Ingot Committee (submitted by the Liquid-Steel Temperature Sub-Committee).)
- H. MORROGH: "The Neutralization of Sulphur in Cast Iron by Various Alloying Elements." (Andrew Carnegie Research Report.)
- J. R. RAFT and H. W. PINDER: "The Origin and Constitution of Certain Non-Metallic Inclusions in Steel."
- R. J. SARJANT: "The Determination of FeO in Steel from the Carbon Drop."
- H. L. SAUNDERS and H. J. TRESS: "An Experimental Enquiry into the Interactions of Gases and Ore in the Blast-Furnace.—Part VI.—Influence of Limestone on the Reduction of Iron Ore at up to 850° C."
- H. L. SAUNDERS and R. WILD: "Distribution in the Gas Producer."
- F. WORMWELL: "The Influence of Movement on the Corrosion of Metals in Salt Solutions and Natural Waters. Part I.—Low-Speed Rotation of Mild Steel: Peripheral Velocities below 100 Ft./Min."
- W. J. WRAŻEJ: "The Structure of Tempered Martensite."
- C. A. ZAPFFE: "Dissociation Reactions Within Inclusions."
- C. A. ZAPFFE: "Neumann Bands and the Planar-Pressure Theory of Hydrogen Embrittlement."
- Special Report No. 32: "Third Report on Refractory Materials." By the Joint Refractories Research Committee of the British Iron and Steel Research Association and the British Refractories Research Association.
- Special Report No. 33: "The Development of Monolithic Dolomite Linings." By the Technical Panel of the Basic Furnace Linings Committee.
- Special Report No. 34: "First Report of the Rolling-Mill Research Sub-Committee of the Iron and Steel Industrial Research Council."
- Special Report No. 35: "Second Report on the Development of Monolithic Dolomite Linings." By the Technical Panel of the Basic Furnace Linings Committee."
- Special Report No. 36: "Symposium on the Hardenability of Steel." Organized by the Technical Advisory Committee of the Special and Alloy Steels Committee (Ministry of Supply) and The Iron and Steel Institute.
- Special Report No. 37: "The Influence of Port Design on Open-Hearth Furnace Flames." By J. H. Chesters and M. W. Thring.

FILM DISPLAY.

A Film Display was given on Wednesday, 13th November, 1946, from 8.0 P.M. to 9.30 P.M., in the Lecture Theatre of The Institution of Civil Engineers, Great George Street, London, S.W. 1. The following films were shown :

"*Open-Hearth Furnace Flames.*" By Dr. J. H. CHESTERS, of The United Steel Companies, Ltd.

A record of flame characteristics and other aspects of the trials and experiments conducted in the open-hearth melting shop at Templeborough (*see* Special Report No. 37).

"*The Control and Prevention of Distortion in Arc Welding.*" Prepared by Walt Disney Productions and released by Lincoln Electric Co., Ltd.

A Disney character—Mr. Shrink—is used to illustrate how to minimize the effects of shrinkage and how to make shrinkage forces work to the welder's advantage.

"*A Photographic Investigation of the Brightness of Liquid-Steel Streams.*" By Mr. J. A. HALL, of the National Physical Laboratory.

A short record of observations made by the National Physical Laboratory.

"*The Measurement of Liquid-Steel Temperatures.*" Prepared by Mr. J. A. HALL, of the National Physical Laboratory, for the Pyrometry Sub-Committee of the British Iron and Steel Research Association.

A record of the technique of the quick-immersion thermocouple, showing the method of assembly and the ways in which it has been applied in different works and types of furnace.

THE FUNDAMENTAL CHARACTERISTICS OF MOULDING SANDS.*

By W. DAVIES, PH.D., M.Sc., F.G.S. (UNIVERSITY OF SHEFFIELD).

(Figs. 1 to 11 = Plates I. and II.)

Paper No. 20/1946 of the Steel Castings Research Committee (submitted by Dr. W. J. Rees, through the Moulding Materials Sub-Committee).

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SYNOPSIS.

Moulding sands may be prepared by mixing sand and clay (synthetic moulding sands) or they may be naturally occurring mixtures of sand and clay (naturally bonded moulding sands). Both synthetic and naturally bonded sands should be composed of two size-grades only, viz., the sand grade and the clay grade, that is, of particles 1.0–0.1 mm. in dia. and particles less than 0.01 mm. in dia. The proportion of grains of other sizes should be small.

The behaviour of a moulding sand in foundry practice depends on its fundamental characteristics, such as : Plasticity, permeability, strength, and refractoriness ; these characteristics are determined by the shape, mechanical grading, and mineralogical constitution of the two grades.

In this paper the geological characteristics are discussed, particularly as regards the mineralogy of the clays. The mechanism of the bonding of moulding sands is reviewed in the light of recent hypotheses ; this is followed by a detailed discussion of the effects of different types of clay on the moulding properties of a sand as a whole.

I.—INTRODUCTION.

THIS paper is based on a thesis submitted to, and approved by, the University of London for the degree of Ph.D. The work was carried out in the Department of Refractory Materials, University of Sheffield, under the general direction and supervision of Dr. W. J. Rees ; the author wishes to express his sincere thanks to Dr. Rees for his direction and for much constructive criticism.

Before the 1914–1918 War, the problem of mould or core fabric for all but the heaviest steel castings was solved with more or less success by the use of naturally bonded sands, such as “Belgian yellow” and “Clyde rotten-rock” sands. These naturally bonded sands were blended with high-silica sand such as that from Leighton Buzzard. Such mixtures provided a more or less satisfactory solution to the problem, but the reasons for their suitability or otherwise received little systematic attention.¹

It was not until the outbreak of war in 1914, when the supplies of Belgian sand ceased and deliveries of French sands became irregular owing to the shortage of shipping space, that the properties of moulding sands received much consideration. In view of the position, Professor P. G. H. Boswell was instructed by the Ministry of Munitions to examine alternative resources of moulding sands in this country. Little systematic work on sands had been published and the literature on moulding sands was extremely contradictory, so Professor Boswell commenced his study by investigating the sands previously used in the foundries.

In that investigation² two types of sand in the mixes then in use were recognized, namely, naturally bonded sands and high-silica sands ; Professor Boswell’s conclusions regarding their characteristics were founded principally on mechanical grading and on the chemical composition of the separated grades. These conclusions were that the naturally bonded moulding sands which gave the best results in the foundry were composed of well-graded sand grains (*i.e.* of grains of uniform size) and clay, with a negligible

amount of silt. The clay portion acts as a bond and its chemical composition resembles that of a siliceous fireclay, though it contains a noteworthy amount of hydrated iron oxide.

The outstanding features of the high-silica sands then in use were the absence of clay and the small proportion of fine sand and silt (*i.e.* of particles less than 0.25-mm. dia.). Essentially, these sands are well graded and are composed almost wholly of quartz ; Professor Boswell concluded that their action in the moulding-sand mixes then in use was to increase the refractoriness and permeability.

During the last twenty years there has been a rapid extension in the use of synthetic sands, that is, of mixtures made by milling a high-silica sand and a clay together. The sands used for this purpose have the same general characteristics as the high-silica sands discussed by Professor Boswell. Since the publication of his work other methods of study have been developed, and Professor Boswell’s conclusions can be modified and expanded. The application of X-ray diffraction technique to the study of clays has made the identification of the mineral constituents possible, and, as a result, the bonding properties of clays can be correlated with their mineralogical constitution.

Stress must also be laid on the shape as well as on the grading of the sand grains. A sand composed of angular grains does not pack around the pattern during moulding so uniformly as does a sand composed of rounded grains. Moreover, the friability of the mould surface, particularly that of dry-sand moulds, increases with increase of angularity of the grains.

As a result of the advances in this and allied fields, the relationship between the geological characteristics of a sand on the one hand and the moulding characteristics, such as plasticity and strength, on the other, can now be discussed in detail. The particular treatment of these fundamental characteristics in the present investigation cannot be final, for fresh advances are continually being made. The outline here given is intended to be more of a synthesis of modern theories ; as

such it may stimulate discussion and perhaps lead to further advances.

This paper is concerned primarily with the part played by the bond in moulding sands. The effects of the size and shape of the sand grains on the moulding characteristics are discussed in separate papers.^{3, 4}

II.—THE MINERAL CONSTITUENTS OF NATURAL AND SYNTHETIC MOULDING SANDS.

The mineral constituents of moulding sands were derived principally from the primary rocks, particularly the acid crystalline rocks such as granite, granite-gneiss, siliceous schists, and quartzites. Certain bonding clays were derived, in part at least, from basic crystalline rocks such as basalt and from pyroclastic rocks such as volcanic ashes. These parent rocks were broken down more or less completely by the processes of weathering or by pneumatolysis. The weathering processes were of two kinds—mechanical and chemical.

Mechanical weathering is brought about by the alternate freezing and thawing of water in crevices in the rocks and by changes in temperature, which set up strains in the rock owing to uneven expansion and contraction; the resultant debris has much the same mineral constitution as the parent rock.

On the other hand, the debris resulting from chemical weathering differs not only chemically but also mineralogically from the parent rocks. The minerals constituting these rocks were formed at high temperatures, and often under considerable pressure. At the temperature and pressure prevailing at the earth's surface, the silicate minerals of these rocks are unstable, particularly in the presence of water and carbon dioxide, and of weak organic acids (humic acids) derived from the decomposition of vegetation. The decomposition of these silicates results in the formation of new silicate minerals which are generally poorer in alkalis and more hydrated than the original minerals; these newly formed silicates are known collectively as "the clay minerals." Hydrated iron oxides, such as limonite, may be set free during the decomposition of the original minerals.

Though weathering provided the bulk of the debris from which sands and clays were formed, pneumatolysis has been the predominant cause of the disintegration of the rocks in certain districts. Steam, carbon dioxide, borates, fluorides, and chlorides, that is, substances which are often evolved by deep-seated igneous intrusions, are among the principle agents of pneumatolysis. The kaolin deposits associated with the granite intrusions of Devon and Cornwall are believed to be due to the action of these agents on the feldspar of the granites.

After the disintegration of the parent rocks by weathering, the resultant debris may be left *in situ*, so forming a "residual deposit", or it may be transported by running water, by wind, or by glaciers, to form a "transported deposit" elsewhere. The kaolin deposits of Cornwall and Devon are typical residual deposits, the quartz, mica, and kaolin resulting from the pneumatolysis of the granites⁵ having been left where they were formed. When the debris is transported and redeposited, there may be some sorting of the constituent grains; the ball-clay series of Devon and Dorset are typical transported deposits.

(1) *The Mineral Constituents of the Sand Grade.*

The sand grade is composed chiefly of mechanically weathered debris. Quartz is the principal constituent; in some sands, feldspar and muscovite form a noteworthy proportion of this grade. Glauconite is an important constituent of certain sands; unlike the other constituents of the sand grade, it is formed from the chemical-decomposition products of the parent rocks, instead of being an original constituent of the igneous rocks. As well as the minerals mentioned, minor constituents—such as zircon, tourmaline, garnet, rutile, kyanite, ilmenite, limonite, and magnetite—may form up to 0.5% of the sand grade. These minor constituents have specific gravities which are distinctly higher than those of the principal constituents; they are therefore known as "the heavy minerals". So far as moulding properties are concerned, the heavy minerals appear to be of little or no importance. Consequently the only constituents of the sand grade that need to be discussed here are quartz, feldspar, muscovite, and glauconite.

Quartz.—The character of the quartz grains in a sand deposit is governed by the nature of the parent rock, by the process of disintegration of that rock, by the mode of transportation, and by changes which occurred subsequent to the accumulation of the deposit.

The quartz grains liberated by the disintegration of granites differ from those liberated by that of the regionally metamorphosed rocks, such as granite-gneiss and siliceous schist. Sorby⁶ pointed out that the quartz grains released from granites by the decomposition of the surrounding feldspars are irregularly angular and tend to be equidimensional; the surfaces of the quartz grains are dull and corroded, owing to the solvent action of the alkalis liberated by the decomposition of the feldspars. On the other hand, quartz grains liberated by the mechanical weathering of granites are usually sharply angular, with clean, glassy surfaces. Typical grains of granitic origin in a quartzose sandstone are shown in Fig. 1.

The quartz grains of the metamorphosed rocks

usually show the effects of shearing and tend to be flattened parallel to the plane of shearing; frequently, several quartz grains are intricately sutured together. The chemical decomposition of the feldspars results in the release of rather oblate quartz grains with corroded surfaces, or of composite grains built up of several sutured grains. When thin sections of the grains are examined microscopically, the effects due to shearing are visible either as permanent deformation (indicated by shadows under crossed nicols) or by slip planes whose traces appear as lines of inclusions traversing the grains, as in Fig. 2. As quartz has no cleavage, the slip planes are the only structural weaknesses along which mechanical weathering can take effect. In most sheared grains the slip planes are closely spaced, consequently mechanical weathering splits the quartz grains into numerous smaller grains, frequently of silt-grade dimensions; in Fig. 3 the grains have split owing to frost action, and some of the fragments are of silt-grade dimensions. In the working of a sand quarry it may be desirable to discard the sand which has been so near to the surface as to be affected by frost, otherwise there may be more silt in the quarry output than is desirable.

This difference between grains derived from granites and those derived from regionally metamorphosed rocks has several practical implications. For example, many naturally bonded moulding sands, such as those prepared from the "rotten rocks" of Durham and Scotland, are milled heavily, as this develops the strength of the bond. Provided that the quartz grains have not been sheared, the milling has little effect on the size of the quartz grains. If the grains have been sheared, the milling tends to crush the grains, thereby increasing the proportion of silt grade. This point is illustrated by a Carboniferous sandstone from the North of England. Examination of the thin section shows that this sandstone contains a noteworthy proportion of quartz grains more than 0.5 mm. across; these grains contain linearly arranged inclusions and show well-marked strain shadows. After heavy milling, the sieve analysis of the crushed material showed that the proportion of grains larger than 0.5 mm. across was negligible.

After a sand deposit has accumulated, it may remain in a comparatively loose, unconsolidated state, e.g. the Lower Greensand of Leighton Buzzard. On the other hand, it may be compacted to form a sandstone such as the quartzitic sandstones of Bwlch Gwyn in North Wales. As a result of the changes leading to the consolidation of the sand, the shape of the quartz grains may be modified. The grains may be corroded by the alkaline solutions derived from the decomposition of feldspar which has survived weathering and transport; local solution of adjacent quartz

grains may occur at their points of contact; the surface area of the grain may be increased by pits produced by corrosion of the grain surface. The shape of the quartz grains may also be modified by secondary silicification, that is, by silica which has been deposited on the quartz grains. This silica is derived from the decomposition of unstable silicate minerals, or from the corrosion of quartz grains elsewhere in the same sand deposit; silica may even be dissolved from one part of a grain and redeposited on another part of the grain. This dissolved silica is probably in the colloidal state and is redeposited as quartz in optical continuity with the quartz grain. In many grains the boundary between this layer of secondary quartz and the original grain can be distinguished by a layer of air bubbles trapped in the junction, or by a coating of limonite or clay on the original grain. Typical examples are shown in Fig. 4.

Feldspar.—In most cases, the minerals of the sand grade have been derived originally from igneous and metamorphic rocks containing quite as large a proportion of feldspar as of quartz, yet few sands or sandstones contain more than 15% of feldspar and less than 70% of quartz.

The elimination of feldspar from the sand grade is due to a combination of mechanical and chemical weathering. The feldspar breaks along the cleavages into small blocks; a typical section of feldspar divided by cleavage cracks is shown in Fig. 5. This process is assisted by the chemical decomposition of the feldspar, as alteration commences along the cleavage cracks, and is accompanied by an increase in volume. The feldspar shown in Fig. 6 is partially decomposed along the cleavage cracks. The feldspar is thereby reduced to particles of silt dimensions or less. Decomposition ultimately leads to the conversion of the feldspar to clay minerals, and even to bauxite.

The conditions governing the decomposition of feldspar were discussed by Mackie.⁷ Under glacial or under hot, arid, conditions, chemical decomposition is at a minimum; consequently sands which have accumulated under these climatic conditions usually contain a high proportion of feldspar. Under humid conditions, chemical decomposition is at a maximum and feldspar is eliminated rapidly.

These observations are of considerable importance, for they imply that the general character of a sand deposit is governed by the climatic conditions under which the sand accumulated. Consequently, the feldspar content of any one sand deposit is usually constant over its whole outcrop. This principle can be illustrated by reference to the famous Bunter moulding sands, so widely used in England for iron-founding, and by reference to some of the "rotten-rock" moulding

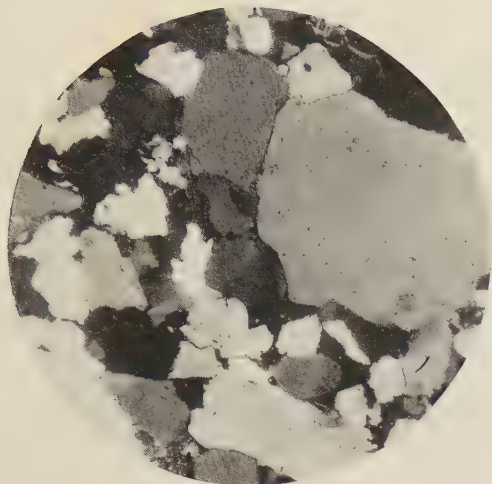


FIG. 1.—Quartzose Sandstone composed of quartz grains of granitic origin; grains enclose a few scattered inclusions. $\times 25$, crossed nicols.

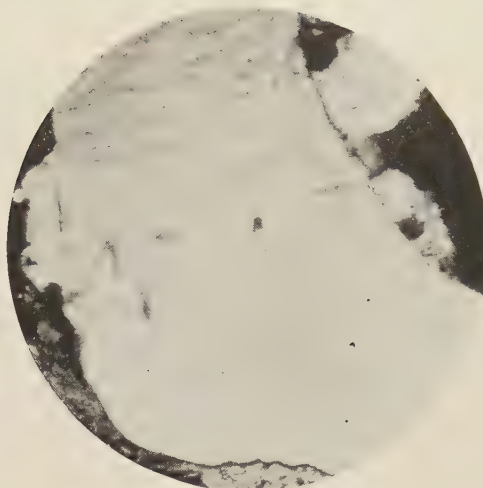


FIG. 2.—Quartz Grain of metamorphic origin; linearly arranged inclusions conspicuous as parallel-like lines across the grain. $\times 100$, crossed nicols.

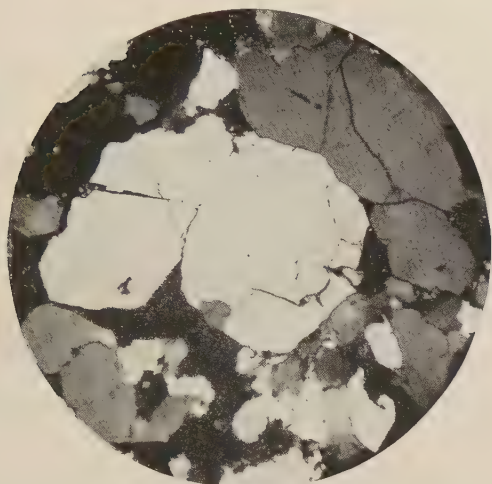


FIG. 3.—Quartz Grains fractured along slip planes by frost action. $\times 25$, crossed nicols.

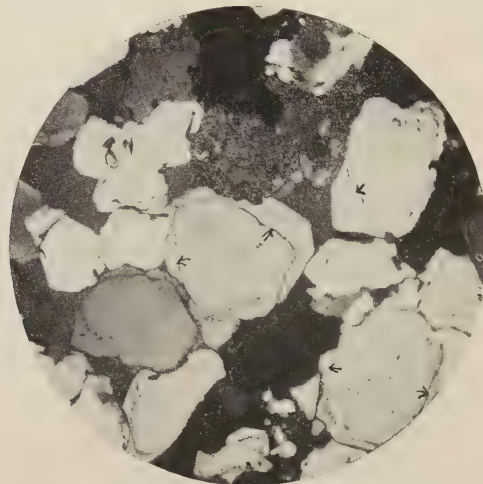


FIG. 4.—Quartz Grains coated by secondary silica. Original outline seen as film of limonite (indicated by arrows). $\times 25$, crossed nicols.



FIG. 5.—Cleavage Cracks in Felspar. $\times 30$, crossed nicols.

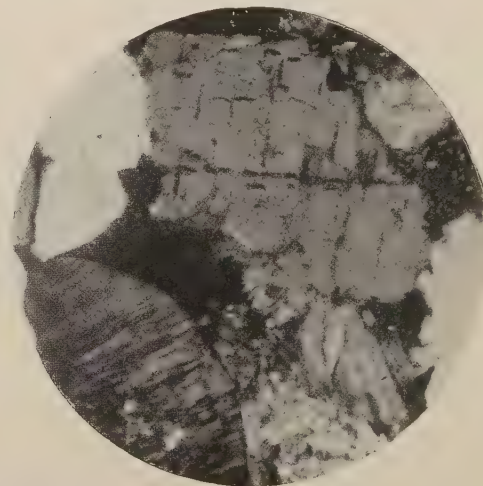


FIG. 6.—Decomposition of Felspar along cleavage cracks. $\times 30$, crossed nicols.

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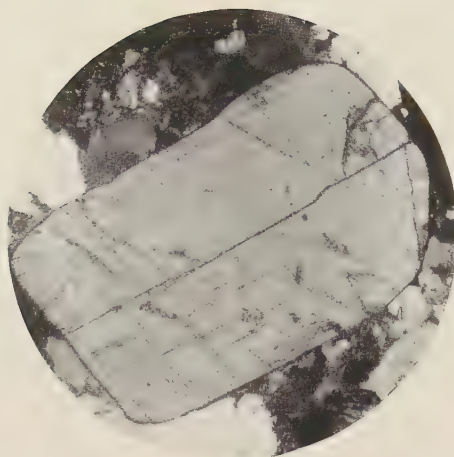


FIG. 7.—Rounded Grain of Microcline Feldspar, showing micropertthitic structure. $\times 50$, crossed nicols. Reduced to four-fifths linear in reproduction.

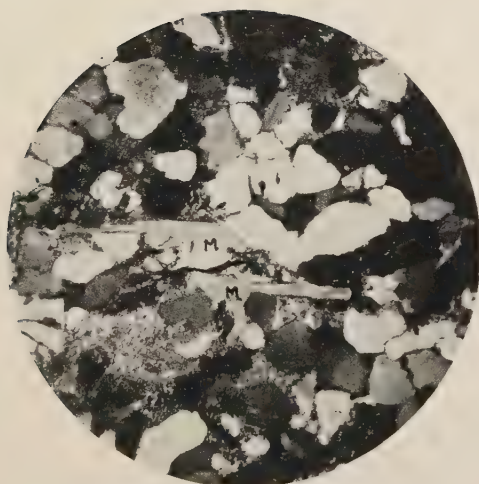


FIG. 8.—Muscovite Flakes (*M*) in a sandstone. $\times 30$, crossed nicols.

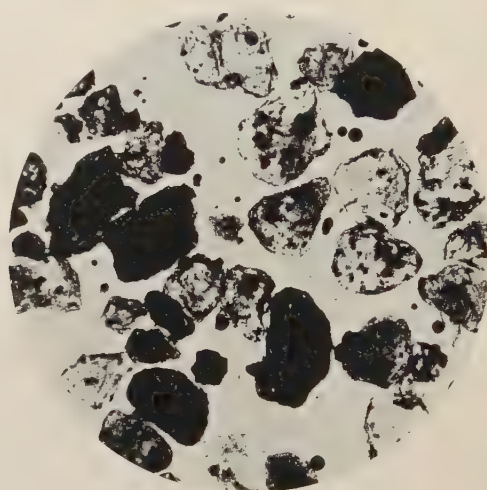


FIG. 9.—South-Cave/Chelford/Bentonite mix. Sand grains before milling.

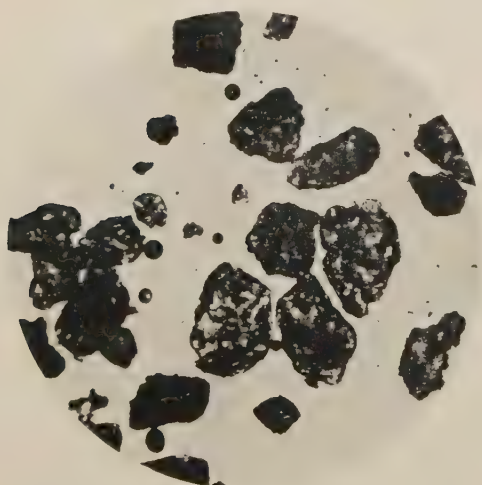


FIG. 10.—South-Cave/Chelford/Bentonite mix. Sand grains after two-minute milling.

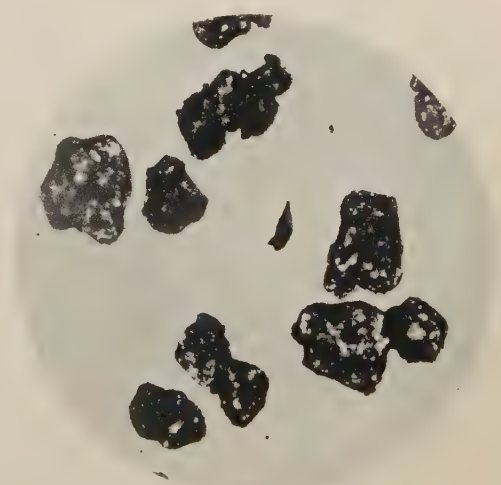


FIG. 11.—South-Cave/Chelford/Bentonite mix. Sand grains after four-minute milling.

sands of the Lowland Valley of Scotland, which are employed in steel-casting.

The Bunter Sands of England were formed under desert conditions; Boswell² (*op. cit.*, p. 146) has pointed out that the potash content of the sands is consistently about 2–3% over the whole outcrop. This potash is largely in the form of feldspar, which would thus constitute 15% of the sand. Consequently the Bunter sands, as a whole, are not sufficiently refractory to be used in bulk for steel-casting, although they can be used in conjunction with other sands.

The Scottish "rotten rocks" accumulated in a humid climate. As a result they contain little or no feldspar, though they contain 10–20% of clay minerals derived from the decomposition of feldspar. These clay minerals contain less alkalis than the parent feldspar and, consequently, some of the "rotten-rock" sands are sufficiently refractory for steel moulding.

The feldspars of igneous or metamorphic rocks are of three main types, *viz.* orthoclase, plagioclase, and microcline. Of these, microcline is the most resistant to chemical decomposition and persists in sediments long after the elimination of orthoclase and plagioclase; it is therefore the typical feldspar constituent of the sand grade. When the microcline is examined in thin section, microperthitic structure (as shown in Fig. 7), due to the intergrowth of a small amount of plagioclase with the microcline, may usually be detected.

Muscovite.—This mica has a flakey tendency and is very resistant to weathering. Many natural moulding sands contain some flakes, which are distributed irregularly through the sand. Typical flakes are illustrated by Fig. 8. Muscovite flakes are very resistant to crushing; instead they shear into thinner flakes which are far too large to act as bonding material. During the ramming of the moulding sand around the pattern such flakes set themselves at right angles to the ramming pressure, and if they are sufficiently abundant they will impart a laminated structure to the mould. Furthermore, muscovite lowers the refractoriness and resistance to sintering. Certain sandstones, such as those in the Coal Measures of Durham, have a flaggy character due to the distribution of muscovite in closely spaced parallel layers; such sandstones are quite unsuitable for moulding work, on account of their high muscovite content.

Glaucinite.—This mineral occurs in abundance in certain sands, especially the Cretaceous Greensands. On the basis of grading it has to be considered as a constituent of both the sand grade and of the clay grade. In the sand grade it appears as rounded or irregular grains which are composed of finely divided or amorphous glauconite. In some varieties the grains show lamellar structure.

During milling, the glauconite grains break down fairly easily and are distributed over the other constituents of the sand grade; consequently it is best considered along with the minerals of the clay grade, particularly as it occurs in a finely disseminated form in certain clays, *e.g.* Chalk Marl and the Chloritic Marl of Cretaceous age.

(2) *The Mineral Constituents of the Clay Grade.*

Essentially, the mineral constituents of the clay grade should act as a bond between the sand grains. Distinction may accordingly be drawn between the constituents which have an appreciable bonding capacity and those whose bonding capacity is slight. The latter group includes quartz, muscovite, feldspar, siderite, iron pyrites, marcasite, calcite, dolomite, gypsum, and carbonaceous matter. The proportion of these constituents in the clay grade should be as small as possible, as they reduce the bonding capacity of the clay grade as a whole. Furthermore, certain of these minerals (notably gypsum and iron pyrites) have low fusion points, and thus lower the refractoriness of a sand containing them. The quartz and muscovite contained in the clay grade differ only in size from their counterparts in the sand grade. The feldspar is usually the fine-grained counterpart of the feldspar of the sand grade; it may also have been formed in certain bonding clays by chemical changes during the deposition and consolidation of the clay.^{8,9} The carbonaceous matter represents the remains of plants. The other minerals were formed for the most part during the accumulation of the sediment.

The constituents which provide the bond between the sand grains are the clay and the limonite minerals; these generally appear in the clay grade as aggregates of extremely minute particles. The internal or atomic structure of these minerals is of the sheet type, which imparts a flaky habit to the minerals and accounts for their basal cleavage. The clay minerals, including glauconite, are essentially hydrated silicates of aluminium, iron, magnesium, calcium, sodium, and potassium. The limonite minerals are composed of hydrated ferric oxide. As the atomic structure of these minerals is of fundamental importance in the discussion of bonding properties, a brief account of their structures is included.

(a) *The Clay Minerals.*

The elucidation of the general structural scheme of the clay minerals is due to Pauling.^{10,11} In 1928 he outlined the principles underlying the structure of ionic crystals and subsequently applied them to certain of the clay minerals. In accordance with these principles, the atoms

constituting the lattice may be regarded as ions with a characteristic electrical charge and a characteristic ionic radius, which determines how closely the ions can be packed. The ions are arranged that the potential energy is at a minimum; this energy is mainly electrostatic. The chemical law of valency is satisfied by making total positive and negative charges equal. Thus each positively charged ion is surrounded by a number of negatively charged ions, and *vice versa*. In other words, there are no "molecules"; instead, the charge on, say, a positive ion is shared equally between the surrounding negative ions.

Pauling recognized that the structures of talc and pyrophyllite, the micas proper,¹² the clintonite micas (the brittle micas), the chlorite micas¹³ (the flexible micas), and kaolinite were based on the same structural units. Pauling's generalizations have been confirmed and extended to the other clay minerals. Their structure is determined by the large size of the oxygen ion relative to those of the common cations such as sodium,

charges; the fourth charge is satisfied by the fourth oxygen ion, which is thus left with an unsatisfied charge—in silicic acid, this is taken up by hydrogen.

The second type is based on the structure of brucite ($\text{Mg}(\text{OH})_2$) and gibbsite ($\text{Al}(\text{OH})_3$). In both these minerals the structural unit consists of two sheets of hydroxyl ions which are arranged in hexagonal close-packing. In brucite, magnesium ions are packed between these two sheets, so that each magnesium ion lies between six OH^- ions.

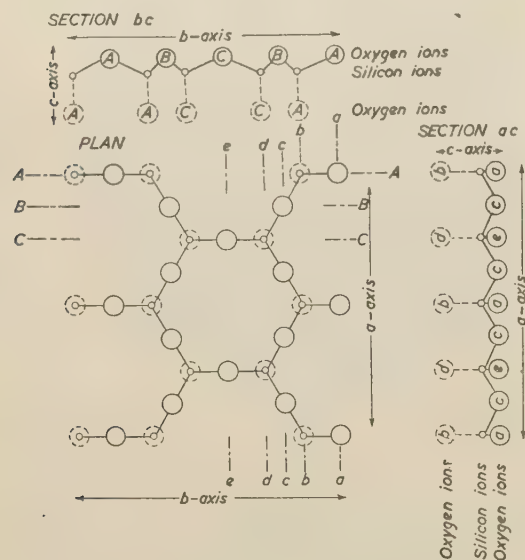


FIG. 12.—Structure of the Silica Layer.

magnesium, iron, aluminium, and silicon. It is so large that the packing together of the ions in the structure is mainly a packing of oxygen ions, with metallic cations in the interstices. The two types of layer structure are involved.

The first type is based on silica tetrahedra, that is, groups of four oxygen ions arranged in tetrahedral fashion and surrounding a silicon ion. These tetrahedra form a layer in which three of the four oxygen ions in each tetrahedra are coplanar; these coplanar ions are shared between adjacent tetrahedra so that each is linked to two silicon ions as shown in Fig. 12.* The coplanar oxygen ions thereby satisfy three of the silicon

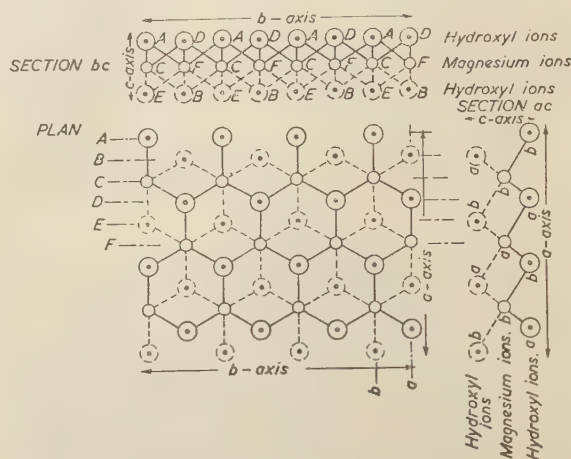


FIG. 13.—Structure of the Brucite Layer.

In gibbsite, two aluminium ions are substituted for every three magnesium ions, that is, two-thirds of the magnesium positions are filled by aluminium ions and the remainder left unoccupied. The brucite and gibbsite structures are shown diagrammatically in Figs. 13 and 14 respectively.

The lattices of various clay minerals differ in the manner in which these two types of structural units are assembled. De Lapparent¹⁴ distinguished three groups of clays on the basis of the thickness of the layer structure, that is, the height of the unit cell. Kerr¹⁵ recognized three groups, which he refers to as the kaolin group, the mont-

*

Key to the symbols in Figs. 12-23.

- = Silicon ion.
- = Aluminium ion.
- = Magnesium ion.
- = Oxygen ion in top sheet.
- = Hydroxyl ion in top sheet.
- = Oxygen ion in bottom sheet.
- = Hydroxyl ion in bottom sheet.

In Figs. 12-15, the letters on or adjacent to the ions in the sections *ac*, *bc*, of the lattices indicate the positions of the same ions in the plans of the lattices. All ions lying on the same line in the plan are indicated by the same letter. Thus, in the plan, Fig. 12, the oxygen ions on lines *a*, *c*, *e* are shown to be coplanar in the section parallel to the crystallographic axes *a* and *c*.

morillonite group, and the alkali-bearing clay minerals. The last-named group corresponds approximately to the "illite" group of Grim,

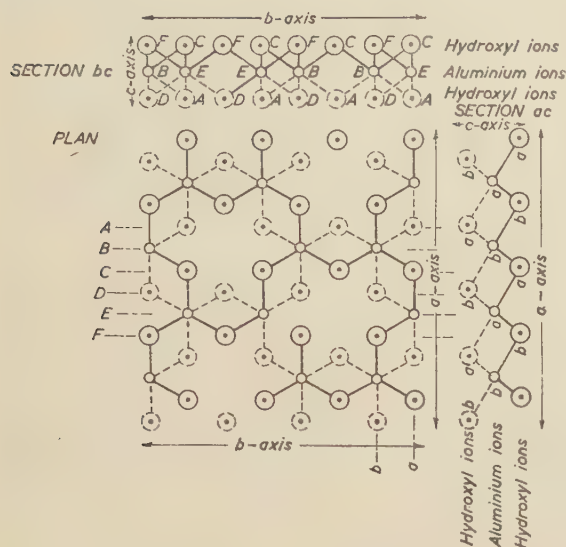


FIG. 14.—Structure of the Gibbsite Layer.

Bray, and Bradley¹⁶; the more general term, "secondary micas" will be employed here. The definition which Marshall¹⁷ gives to "beidelite" allies this mineral to the secondary mica group.

The Kaolin Group.—In the minerals in this group the structural unit is formed by the linkage of a silica layer to a gibbsite layer. The unsatisfied oxygen ions of the silica layer in effect replace two-thirds of the hydroxyl ions on one side of the gibbsite layer, so producing the structure shown in Fig. 15.

There are four minerals in this group which have the chemical constitution $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, namely, dickite,* kaolinite, nacrite, and halloysite†; Pauling¹³ first proposed a structural scheme for kaolinite in his paper on the chlorites. Gruner¹⁸ confirmed this scheme and subsequently suggested similar schemes for dickite¹⁹ and nacrite.²⁰ Mehmel²¹ showed that the structure of halloysite was closely allied to that of kaolinite. The four minerals differ in the manner in which successive structural units are stacked on one another, as shown in Fig. 16 (a to e). The stacking arrangement in kaolinite was confirmed by Hendricks,²² while that for dickite was confirmed by Ksandra and Barth,²³ and later by Hendricks (*loc. cit.*, p. 170). These authors suggest alternative arrangements of the anions

and cations in the sheets composing the structural units.

Pauling¹³ assumed that the units were polar, with the hydroxyl groups of one unit in contact with the coplanar oxygens of the silica layer of the adjacent unit. Such a structure explains the very perfect cleavage of these minerals.

Kaolinite is closely allied to another clay mineral, *viz.*, anauxite.²⁴ Though the latter has the same general structure, its chemical constitution is rather different. The type mineral, from Bilin in Czechoslovakia,²⁵ has the constitution

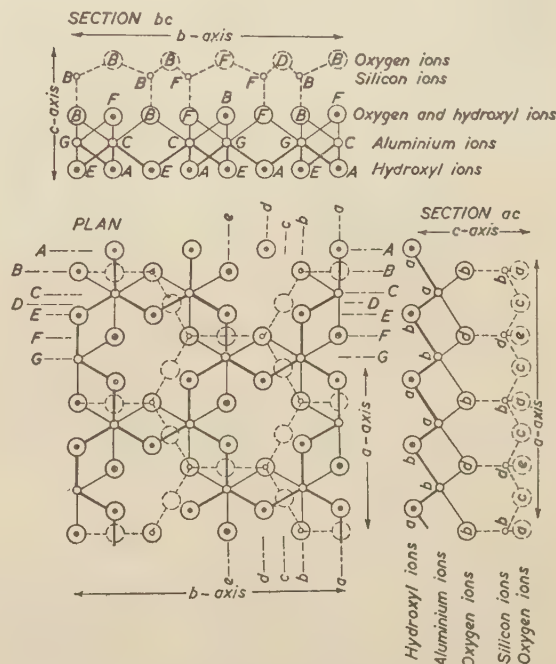


FIG. 15.—Structural Unit in the Kaolinite Group. The silica layer is shown by broken lines, the gibbsite layer by continuous lines.

$\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, that is, it contains more silica than kaolinite. The manner in which the increase in the Si/Al ratio occurs is still a matter for discussion; Gruner²⁶ originally suggested that Si^{++++} ions replaced some of the Al ions in the gibbsite layer, thereby postulating Si with a covalency of six; Bragg¹¹ doubted this hypothesis, as it is so much at variance with other silicate structures. Hendricks²⁷ later suggested that certain of the Al^{+++} and OH^- ions were lacking from the gibbsite layer of the structure, thereby increasing the ratio of Si ions to Al ions. Finally, Gruner²⁸ came to the conclusion that SiO groups could be substituted for $\text{AlO}_2(\text{OH})_4$ groups in the gibbsite layer. It therefore appears that

* "Dickite" is the name proposed by C. S. Ross and P. F. Kerr²⁴ for the mineral occurring at Amlweh, Anglesey, and described by A. Dick as "kaolinite" (*Mineralogical Magazine*, 1888, vol. 8, p. 15; *ibid.*, 1908, vol. 15, p. 124). Ross and Kerr defined kaolinite as the clay mineral of kaolin or china clay.

† Halloysite, as used here, is the same as the metahalloysite of M. Mehmel;²¹ "hydrated halloysite", in the present paper, is the same as the "halloysite" of Mehmel (*loc. cit.*).

anauxite forms a series with kaolinite in which the Si/Al ratio can vary, though the lattice remains fundamentally the same as that of kaolinite. Chemical analyses of anauxite show the presence of a small amount of ferric iron, which apparently replaces some of the Al ions in the gibbsite layer.

P. F. Kerr¹⁵ also includes the mineral allophane in the kaolin group. Allophane has the chemical constitution $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ and is structureless, being comparable in many ways with opal. It occurs in association with halloysite. According

to clay and ball clays of the south of England. Halloysite and metahalloysite are produced from aluminous materials by the action of sulphuric acid derived from the decomposition of pyrites; they are commonly associated with kaolinite as, for instance, at Liège in Belgium. Anauxite appears to be formed in the same way as kaolinite, but the aluminous material from which it was derived probably contained more silica than would be required for the formation of kaolinite. Nacrite and dickite are formed by hydrothermal activity, possibly at higher temperatures than in the case of kaolinite.

The Montmorillonite Group.—The terminology applied to this group is rather confused. The classifications given by Kerr,¹⁵ Nagelschmidt,³⁰ Marshall,¹⁷ and Grim,³¹ differ in detail. All are agreed that the structural unit in this group is essentially that of a gibbsite layer between two silica layers. The two silica layers are attached to the gibbsite layer in the same way as the single

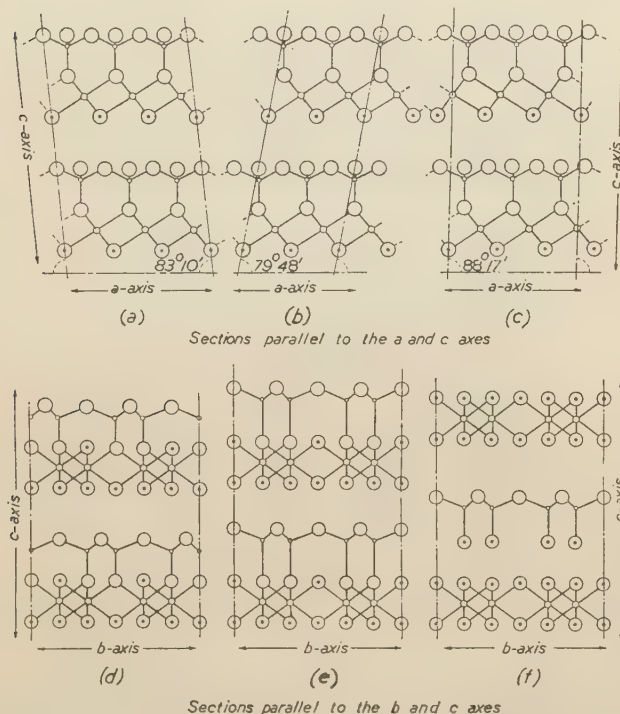


FIG. 16.—Stacking of the Structural Units in (a) dickite; (b) kaolinite; (c) nacrite; (d) kaolinite; (e) halloysite; (f) hydrated halloysite. ((a), (b), and (c) show sections parallel to the a and c axes; (d), (e), and (f) show sections parallel to the b and c axes.)

to Ross and Kerr,²⁹ allophane is a mutual solution of silica, alumina, and water.

Hydrated halloysite^{21, 22} is a low-temperature mineral allied to the other minerals of the kaolin group. On heating to 50° C. it changes to halloysite, with the loss of $2\text{H}_2\text{O}$. Mehmel²¹ suggested the structure of hydrated halloysite shown in Fig. 16(f). Hendricks²² (*loc. cit.*, p. 170) suggested that the mineral has alternate halloysite and $2\text{H}_2\text{O}$ layers rather than separate gibbsite and hydrated silica layers, as suggested by Mehmel.

Kaolinite is derived from the alteration of feldspar or other aluminous material by chemical weathering or by hydrothermal activity; it is the principal clay-mineral constituent of the china

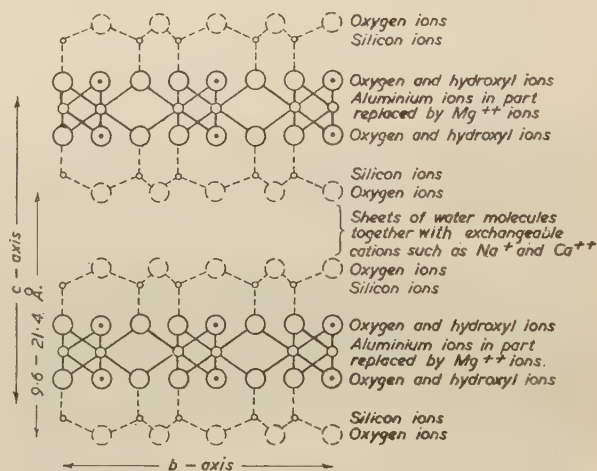


FIG. 17.—Structure of Montmorillonite.

silica layer is attached to the gibbsite layer in the kaolin group (Fig. 15). This structural unit is the same as that proposed by Pauling.¹² In the montmorillonite group the units are arranged in stacks with a variable number of water molecules between the successive units so that the distance c , (Fig. 17), between the corresponding planes in successive units may vary from 9.6 Å to 21.4 Å or even more,^{32, 56} consequently these minerals are said to have an expanding lattice. This behaviour is in marked contrast to that of the kaolin minerals, which do not have an expanding lattice. Grim³³ has suggested that the kaolinite lattice does not expand because of the attraction between the oxygen and hydroxyl sheets, which are adjacent when kaolinite units are stacked one above the other (see Fig. 16(a)), whereas the units in the montmorillonite group are stacked so that the

oxygen sheets are adjacent (Fig. 17). This is why the kaolin minerals do not readily break down in the presence of water into such small flakes as do the montmorillonite minerals.

Though the stacking arrangement just described forms the basis of the montmorillonite group of all four authors, beyond this point differences appear. The structure just described corresponds to Nagelschmidt's definition of montmorillonite proper, and to Kerr's definition of beidellite.

If Fe^{+++} ions are substituted for Al^{+++} ions, then the structure is that of nontronite as defined by Nagelschmidt. Finally, if brucite is substituted for gibbsite in the structural unit, the structure corresponds to that of Nagelschmidt's magnesium beidellite.

Nagelschmidt's recognition of the end-members, montmorillonite, nontronite, and magnesium beidellite, is rather artificial, as it ignores the fact that the structural units in the minerals of the montmorillonite group carry an excess negative charge. This excess charge is due to the substitution of Mg^{++} ions for some of the Al^{+++} ions in the gibbsite layer, so that the total number of ions is unchanged. On applying Pauling's principles governing ionic structures it will be seen that the lattice acquires an excess negative charge, the origin of which is at the centre of the unit. This charge is sufficient to hold other cations at the upper and lower surfaces of each unit; these surface cations are loosely held and differ from the other cations in the lattice in that they are exchangeable, so giving rise to the type of base-exchange postulated by Marshall¹⁷ and by Hofmann and Bilke.³⁴ Among the ions which may occupy these surface positions are sodium, potassium, magnesium, calcium, and hydrogen. The resultant structure is shown in Fig. 17 and corresponds to the montmorillonite structure of Marshall and of Grim. According to the nature of the surface cations, the complete structure is known as sodium montmorillonite, calcium montmorillonite, and so forth. If Mg^{++} ions are substituted for all the Al^{+++} ions, this limiting modification corresponds to the mineral "saponite", as defined by Grim and Kerr, and has the constitution $2\text{MgO} \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$. The substitution of Fe^{+++} ions for some of the Al^{+++} ions in montmorillonite gives rise to the "nontronite" of these authors.

Sodium montmorillonite is the principle clay-mineral constituent of Wyoming Bentonite, while calcium montmorillonite is that of untreated fuller's earth (Fulbond No. I), used in Britain as a bonding clay. Montmorillonite has been identified as one of the chief soil colloids.

The Secondary Micas.—The minerals in this group are not so well defined as in the other two groups, being difficult to isolate for examination. They are derived from the silicate minerals of the

crystalline or primary rocks. The decomposition products of these silicate minerals have much in common with the micas, muscovite and biotite. Like them, they have a flakey structure and cleave readily; they differ in being more highly hydrated than the primary micas and in the detailed arrangement of their atomic structures. As these micaceous decomposition products are important constituents of the sedimentary or secondary rocks they are known as the secondary micas, to distinguish them from the micas (muscovite and biotite) which are constituents of the primary rocks. Grim, Bray, and Bradley¹⁶ have proposed the term "illite" for the clay-mineral constituent of argillaceous sediments belonging to the mica group. The secondary micas are of particular interest, as they form the bond of many of the Carboniferous "rotten rocks" of Durham and Scotland.

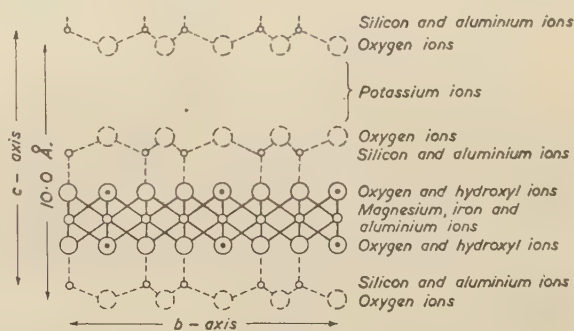


FIG. 18.—Structure of Muscovite.

Two series of secondary micas may be distinguished; the members of the first series are derived primarily from feldspar and also from muscovite; these secondary micas contain little magnesium or iron.

The members of the second series are derived from the ferromagnesian minerals such as biotite, hornblende, and augite; they contain a noteworthy proportion of iron and magnesium.

When feldspar breaks down, secondary micas (known collectively as "sericite") are formed as intermediate stages in a series whose ultimate product under temperate conditions is a member of the kaolinite group³⁵ and under tropical conditions is bauxite. Muscovite becomes more highly hydrated³⁶ when subject to weathering and yields the secondary mica "damourite".³⁷ Both sericite and damourite are structurally allied to muscovite. The structure for muscovite was first proposed by Pauling,¹² though Jackson and West³⁸ suggested the same structure independently a few months later. The structure of muscovite is shown in Fig. 18. Basically the structure is that of a gibbsite layer between two silica layers, in which one in every four Si^{++++} ions

is replaced by an Al^{+++} ion, thereby leaving a negative charge on the lattice; this form of substitution corresponds to that mentioned in Marshall's definition of beidellite.¹⁷ The excess negative charge is neutralized by K^+ ions at the surface of each modified unit; unlike the surface cations in the montmorillonite group, these surface cations are tightly held and consequently the unit layers of the lattice do not expand. In

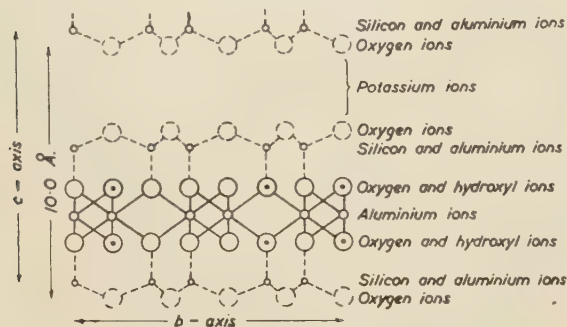


FIG. 19.—Structure of Biotite.

sericite and damourite, the replacement of Si^{++++} ions by Al^{+++} ions is not so extensive as in muscovite, consequently, these two secondary micas hold fewer K^+ surface cations. Though the total of oxygen and hydroxyl ions in the members of the sericite-damourite series is the same as in muscovite, the ratio of hydroxyl to oxygen ions is higher than in muscovite.³⁹

The second, or ferromagnesian, group of secondary micas is structurally allied to biotite. Pauling,¹² in his study of the micas, suggested the structure shown in Fig. 19; the structure differs from that of muscovite in the central layer of the lattice. Instead of a gibbsite layer between two silica layers, as in muscovite, the structure is built up of a brucite layer between two silica layers. As in muscovite, one in every four Si^{++++} ions is replaced by an Al^{+++} ion, thereby leaving an excess charge on the lattice; this charge is neutralized by K^+ ions at the surface of each modified unit. Fe^{++} ions may replace some of the Mg^{++} ions, and 2Fe^{+++} ions may replace 3Mg^{++} ions in the brucite layer, so giving biotite its ferromagnesian character. In the ferromagnesian secondary micas the ratio of the hydroxyl ions to the oxygen ions is higher than in biotite, just as the sericite-damourite micas contain more hydroxyl ions than does muscovite; similarly their potash content is less than that of biotite. Brammall and Leech³⁹ refer to these ferromagnesian secondary micas as hydrobiotite.

Denison, Fry, and Gile³⁶ concluded that when muscovite and biotite are subject to weathering the potash content gradually decreases, while the hydroxyl content gradually increases. Two other decomposition products of biotite have been

recognized as vermiculite and chlorite; the latter mineral is also formed by the breakdown of augite and hornblende—constituents of the primary rocks. According to McMurchy⁴⁰ chlorite is built up of alternate mica-like and brucite-like layers, as predicted by Pauling.¹³ The mica-like layers have the structure of the secondary ferromagnesian micas, while the brucite-like layers resemble the brucite unit, though Al^{+++} ions may replace a proportion of the Mg^{++} ions. The structure is represented in Fig. 20. According to Gruner⁴¹ the structure of vermiculite is allied to that of chlorite, but mica-like layers alternate with $8\text{H}_2\text{O}$ layers, as shown in Fig. 21; the general structure was confirmed by Hendricks and Jefferson⁴²; later the structure of the water layers was discussed in detail by the last-named workers.⁴³ It is commonly observed that biotite is first replaced by vermiculite and then, as alteration proceeds, by chlorite. Gruner uses the term "hydrobiotite" to designate interstratification of biotite layers with vermiculite layers but, as far as the present account is concerned, the term (hydrobiotite) will be employed in the sense used by Brammall and Leech,³⁹ that is, that hydrobiotite is allied to biotite but contains less potash and more hydroxyl.

Gruner⁴⁴ showed that glauconite has a structure

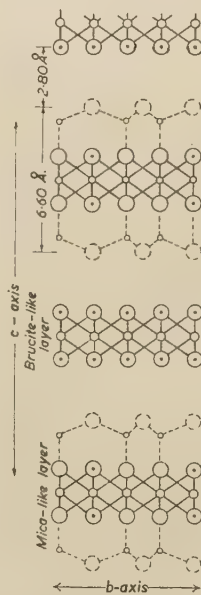


FIG. 20.—The Sequence of Layers in Chlorite.

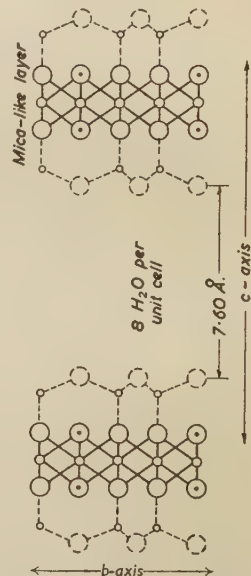


FIG. 21.—The Sequence of Layers in Vermiculite.

closely resembling that of biotite. Glauconite has a higher Si/Al ratio than biotite, because fewer of the Si^{++++} ions in the silica layers have been replaced by other ions, and because the Si^{++++} ions may be replaced by Fe^{+++} ions instead of Al^{+++} ions. Glauconite seems to be formed under marine conditions, particularly in the presence of organic

matter⁴⁵; the details of its formation are still a matter for discussion. Some glauconite may be formed by the decomposition of biotite.⁴⁶

The Base-Exchange Properties of the Clay Minerals.—When one or other of the clay minerals is left in contact with an aqueous solution of, say, sodium chloride, there is an exchange of certain cations of the clay mineral for those of the solution; in this case sodium ions become attached to the clay mineral, and at the same time the chemical equivalent of some other ion will leave the clay and enter the solution. This property of the clay minerals is known as base-exchange.

According to Grim,³³ the base-exchange capacity for the three groups of clay minerals is as follows :

	Milli-equivalents/100 g.
Kaolinite group	3-15
Montmorillonite group	60-100
Secondary-mica group	20-40

Two hypotheses concerning the mechanism of base-exchange have been advanced. Both agree in distinguishing those ions which can be exchanged from those which cannot be exchanged. The ions which are not involved in base-exchange are those which are essential to the lattice structure; for instance, in montmorillonite the silicon ions in the silica layers and the aluminium and magnesium ions in the intervening layer cannot be exchanged.

According to Kelley and Jenny,⁴⁸ there are excess charges at the broken edges of each sheet-like unit; these excess charges are satisfied by other cations which are exchangeable. The kaolin minerals occur as comparatively large crystals, built up of a number of units so that the majority of the hydroxyl sheets are not exposed at the surfaces of the crystals. When kaolinite is subject to fine grinding its base-exchange capacity is increased because more hydroxyl sheets are exposed and because the sheets are fractured, so increasing the proportion of broken edges. They consider that the base-exchange capacity of the minerals of the montmorillonite group is due to cations attached to the lattice edges; as montmorillonite crystals are much smaller than kaolinite crystals there is a far higher proportion of lattice edges and, consequently, montmorillonite has a much greater base-exchange than kaolinite and its allies.

On the other hand, Marshall,¹⁷ followed by Hofmann and Bilke,³⁴ considers that exchangeable cations are those occurring between the successive units, as already described in the present paper; these cations become accessible when water is present, owing to the expansion of the lattice. Marshall⁴⁹ showed that fine grinding does not simply cleave the crystals in their planes of weakness, but breaks and distorts every part of the lattice; thus the comparison of the base-

exchange capacity of the ground and unground materials is not necessarily the comparison of the same material in different states of division, but may actually be the comparison of different minerals.

Probably the mechanism of base-exchange involves both hypotheses.

(b) *The Limonite Minerals.*

Though many text-books on mineralogy list a series of hydrated ferric oxides, Posnjak and Merwin⁵⁰ consider that the only existing hydrate is ferric oxide monohydrate. This occurs in nature in two polymorphic forms—lepidocrocite

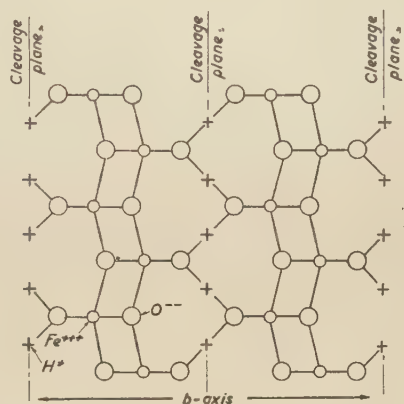


FIG. 22.—Structure of Lepidocrocite.

and goethite; limonite itself is very finely divided goethite.

Ewing⁵¹ found that lepidocrocite has a layer structure composed of three sheets of oxygen ions with the iron atoms so arranged that each is surrounded by six oxygen ions; the structure is shown in Fig. 22. Limonite appears to be a variety of goethite, as the X-ray diffractions

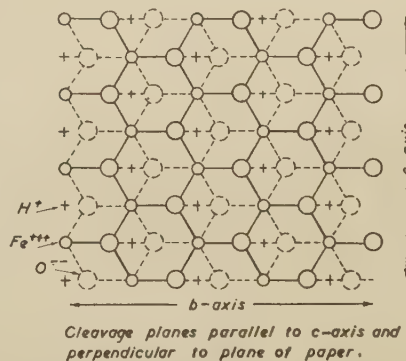


FIG. 23.—Structure of Goethite.

patterns of these substances are similar. According to Goldshtaub,⁵² the oxygen atoms in goethite are arranged in sheets in hexagonal close-packing, with each of the iron atoms surrounded by six

oxygen atoms; the structure is shown in Fig. 23. Both lepidocrocite and goethite cleave readily, in flakes or plates parallel to the layer structure.

III.—THE MOULDING CHARACTERISTICS OF SANDS.

Professor Boswell's analysis of the characteristics of moulding sands was primarily geological, as he was concerned with the geological problem of searching for alternative sources of moulding sands. The ultimate test of any moulding material is necessarily its behaviour in actual foundry practice; the characteristics of a moulding sand which are of immediate importance in this respect depend on the type of foundry practice involved and are not necessarily the same as those employed by the geologist.

Green Sand.—In green-sand practice, the strength of the green (*i.e.* moist) sand, after ramming around the pattern, must be sufficient for the mould to retain its shape during handling. Furthermore, the mould surface must resist the wash of molten metal; in other words, the sand must retain sufficient strength over a wide range of temperature, otherwise sand from the mould surface will find its way into the casting. The heat of the molten metal drives off the moisture from the adjacent sand; if the sand is not sufficiently permeable, the mould surface will crumble, with unfortunate consequences for the casting. The skin imparted to a green-sand casting depends partly on the permeability and the refractoriness of the sand and partly on the weight of the casting; a sand may be quite satisfactory for light castings but not for heavy castings, because, with the latter, it requires to be maintained at high temperature for a longer period. The skin imparted to a casting depends to a large extent on the capacity of the sand to pack to uniform density during the shaping of the mould; this characteristic has been referred to as "plasticity", "flowability", "ramability", and "mould hardness" by different workers.

Though green-sand moulds should be closed and the metal cast shortly after ramming, it frequently happens that the moulds stand for several hours before closing. Some varieties of green sand dry more quickly than others under the ordinary atmospheric conditions prevailing in the foundry, and so are less resistant to the wash of the molten metal.

The sand must retain its strength until the casting no longer requires support and it should then become weak, to facilitate knocking out.

Finally, the re-use of the sand after it is knocked out of the box has to be considered. The bond in green-sand mixes loses some of its combined water, owing to the heat of the molten metal, and that adjacent to the casting is per-

manently dehydrated; further away the bond is not permanently dehydrated and regains its strength on tempering with water. Permanent dehydration occurs more readily with some bonds than with others, that is, some bonds are less durable than others.

Dry Sand.—In dry-sand practice the factors involved are much the same as in green-sand practice. The principle object of drying the mould is to increase its strength (the strength of a dry-sand mould is usually several times as high as that of the same mould in the green state, and consequently the mould surface is more resistant to the wash of the molten metal). With the dry-sand mould, far less moisture is driven off during casting, so that the tendency for the mould to "scale" is reduced. Permeability is important as a factor in the drying of the mould; a more permeable mould dries out more quickly than a less permeable one. For example, Fig. 24

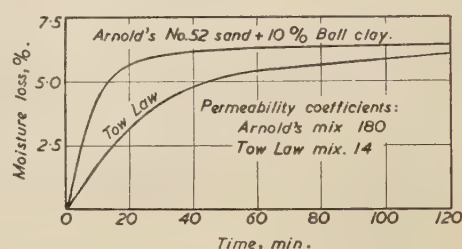


FIG. 24.—Rate of Drying in Relation to Permeability. (Both mixes contained 6.6% of moisture; after ramming into A.F.A. test-pieces, they were dried at 200° C.)

shows the loss of moisture of two A.F.A. test-pieces containing the same moisture initially and dried under the same conditions; Arnold's mix was more permeable than the Tow Law mix, and it dried out more quickly.

In order to obtain the full advantage of the added strength of dry-sand moulds, the casting should be poured as soon as possible after the mould is removed from the drying stove, because the bond is more or less hygroscopic. Though the absorption of moisture by the mould may only be superficial, it may make the mould surface so weak that it is removed by the wash of the molten metal during casting.

Thus the behaviour of a moulding sand in actual foundry practice is determined principally by its plasticity, strength, permeability, and refractoriness. As much foundry work departs from the ideal, the hygroscopic characteristics of the bond must also be taken into account. From the economic standpoint, the durability of the material, that is, the extent to which it can be re-used, is of great importance. All these properties

may be regarded as functions of a system involving three components, namely, the sand grade, the clay grade, and moisture.

(1) *The Bond Structure of Moulding Sands.*

The first aspect of this three-component system to be considered is the mechanism whereby the moulding sand has both plasticity and strength. Although this mechanism has yet to receive detailed theoretical treatment, certain conclusions may be drawn concerning the relationship of lattice structure to bonding properties.

The minerals which act as bonds are characterized by layer lattices which enable the minerals to part readily into flakes; these flakes possess attractive forces of varying intensity, which tend to hold the individual flakes together. These attractive forces may be regarded as acting principally through the flat surfaces of the flakes; the forces at the periphery of a flake are less important.

Clay becomes plastic and exhibits bonding capacity only in the presence of liquids which contain OH^- groups and H^+ ions, such as water, alcohol, and acetic acid; such plasticity cannot be obtained with non-polar liquids such as petrol and benzene. When a clay is in the plastic condition, the surfaces of the flakes are 10^3 – 10^4 Å apart, that is, the flakes are separated by films of liquid, which are often assumed to be highly viscous.⁵³

This film, usually a water film, has several functions. It separates the flakes and thus reduces the attractive force between adjacent flakes, as this force is inversely proportional to the square of the distance between the flakes. In this respect, it is of interest to compare the behaviour of china clay and ball clay, the characteristics of which are later discussed. X-ray diffraction patterns show that the two clays are composed essentially of the same clay material. One distinction may be made. The lines in the ball-clay pattern are more diffuse and indefinite than those of the china-clay pattern, owing to the more finely divided state of the kaolinite in the ball clay. It is a matter of common observation that ball clay is highly plastic whereas china clay is relatively non-plastic; in other words, the films are more numerous in a given mass of ball clay than in a similar mass of china clay.

Marshall⁴⁹ considers that an essential feature of this lubricating action is that the film is composed of orientated molecules, which are generally water dipoles. In this connection the work of Bradley, Grim, and Clark⁵⁴ is of interest. It has already been remarked that montmorillonite has an expanding lattice owing to the entry of water between successive layers in the lattice. The authors just mentioned concluded that the water enters the lattice as complete layers, about 3 Å thick, composed of dipoles; the distance between

the adjacent layers increases in steps of about 3 Å, from 9.6 Å, to 12.4 Å, 15.4 Å, 18.4 Å, and finally to 21.4 Å, corresponding to the entry of one, two, three, and four layers of water. On the other hand, Magdefrau and Hofmann,⁵⁵ followed by Nagelschmidt,⁵⁶ concluded that the spacing varies continuously as a function of the water content.

The Structure of the Water Film.—The fact that a polar liquid is necessary for the development of plasticity in a clay, in conjunction with the conclusions from the work of Marshall,⁴⁹ and of Bradley, Grim, and Clark,⁵⁴ suggests that water molecules in the vicinity of clay minerals are arranged in a definite pattern. This pattern should be of the sheet type. Hendricks and Jefferson⁴³ have discussed the pattern of water molecules in these sheets, both between the successive structural units in the clay-mineral lattices and on the surfaces of clay minerals. They concluded that "the water molecules are arranged in layers in which the molecules are joined into hexagonal groups of an extended hexagonal network". The structure of this network is shown in Fig. 25. It is founded on the

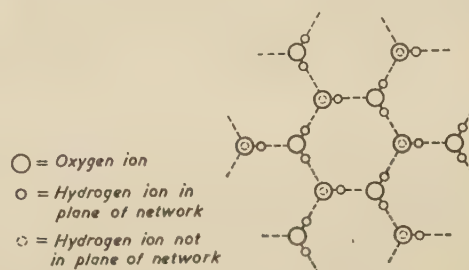


FIG. 25.—Hexagonal Network of Water Molecules (Hendricks and Jefferson).

tetrahedral distribution of charge about a water molecule in the manner discussed by Bernal and Fowler.⁵⁷ Two corners of the tetrahedron are occupied by hydrogen atoms, and the other two corners by an excess of electrons; that is, two of the corners are positively charged, and two are negatively charged. Each side of the hexagons in Fig. 25 corresponds to a hydroxyl bond, the oxygen-hydrogen bond of one tetrahedron being directed towards the negative charge of the adjacent tetrahedron. This accounts for the relationships of three-fourths of the corners of the tetrahedra. In each hexagon in Fig. 25, each of the remaining corners is directed above or below the plane of this hexagonal network. In any hexagon of the network, three of these remaining corners will have negative charges, while the other three will have hydrogen ions, *i.e.*, positive charges. By itself, this network is unstable; it is, however, fairly stable when close to the silica layer of one or other of the clay minerals. Reference to

Figs. 15 to 20 will show that the outermost sheet of the silica layer is composed of oxygen ions. The stability of the water layer is due to the attraction between the hydrogen ions at the fourth corners of the tetrahedra and certain of the oxygen ions of this outermost sheet, as shown in Fig. 26. After the attachment of the first layer of

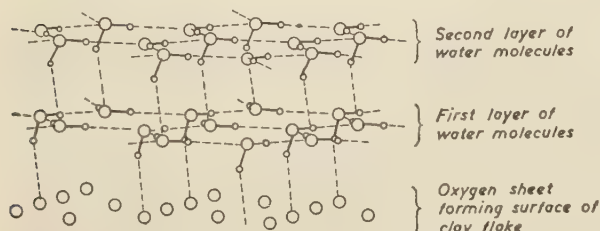


FIG. 26.—Probable Structure of Water Layers attached to Clay Flake (Hendricks and Jefferson).

water molecules in this way, a second layer may be attached to the first by the attraction between the positively charged fourth corners of the tetrahedra in the second layer and the negatively charged fourth corners of the tetrahedra in the first layer, as shown in Fig. 26. In the kaolinite structural unit (Fig. 15), one surface of the unit is a sheet of hydroxyl ions; in this case the negatively charged fourth corners of the water layer are attracted by certain of the ions in the hydroxyl sheet.

This discussion can be applied to the structure of the water films between the clay flakes. Each flake is composed of a number of parallel structural units of the kaolinite, montmorillonite, or secondary-mica type. To the outermost oxygen or hydroxyl sheet of each flake is attached a water layer. To each of these water layers are attached successive water layers, as shown in Fig. 27. The layers near the flake will be fairly complete, but further away the arrangement of

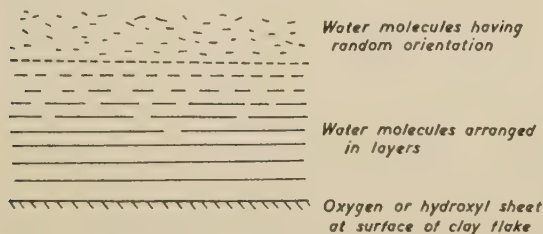


FIG. 27.—Orientation of Water Molecules near the surface of a Clay Flake.

the water molecules in a hexagonal network will become less and less complete, because the stability of the network will decrease as the distance from the clay flake increases.

When clay is in the plastic state, the surfaces of the flakes are of the order of 10^3 – 10^4 Å apart. Thus, if all the molecules in the water films are

arranged in these hexagonal networks, there would have to be upwards of 300 layers (assuming that each has a thickness of about 3 Å). When the clay is very stiff, the water films are so thin that all the molecules are arranged in layers and the water is then in the condition which some workers have described as “highly viscous”. As the moisture content is increased, the water films become thicker and the layers midway between the flakes become progressively easier to displace; in other words the clay becomes more plastic. Ultimately a stage is reached at which the films are so thick (probably greater than 10^4 Å), that further additions of water molecules assume a random orientation; this stage probably corresponds to the “sticky point” of the clay (the stage at which the clay feels sticky when handled).

The structure of the water films in limonite-bonded sands remains to be considered. It is probable that the water films around the flakes of the limonite minerals have much the same pattern as those around clay minerals. Since the limonite minerals have a positive surface charge, the negatively charged fourth corners of the water layer will be attracted by the surface layer of the limonite flakes. The attractive forces between the adjacent flakes of the limonite minerals are higher than those between the adjacent flakes of the clay minerals, consequently layers are more extensively developed in the films around limonite flakes than in those about clay minerals.

It is commonly observed that sands with a limonite-rich bond have a wider moisture range between the point at which they are just moist enough to cling together and the point at which they become sticky than have synthetic sands bonded with, say, ball clay. This is probably accounted for, in part at least, by the more extensive development of layers in the water in the limonite bond; in other words, the water films in limonite can attain a greater thickness before the molecules cease to arrange themselves in layers.

(2) The Milling of a Moulding Sand.

The concept of a clay as a mass of quasi-parallel flakes separated by water films forms the basis of the discussion of the cohesive and plastic properties of moulding sands. When a sand and clay are milled together, each sand grain becomes evenly coated with clay. Once the grains are evenly coated further milling has little or no effect on the strength of the mixture. This is illustrated by a series of tests conducted with an edge-runner mill (revolving-pan type) at a local foundry. The mix used was :

South Cave sand (limonite bonded)	25%
Chelford sand	75%
Bentonite	+3%
Water	+3–4%

Samples were taken from the mill at intervals during the normal milling period of 4 min., and also during an exceptionally long milling period of 20 min.. The South Cave sand is naturally bonded, and, in the photomicrograph (Fig. 9) showing the appearance of the sand grains before milling was commenced, the grains of this sand are opaque, owing to their heavy coating of limonite, while the grains of the Chelford sand are transparent. After milling for 2 min., the Chelford grains were partly coated with bentonite and limonite, thus becoming partly opaque (Fig. 10). After milling for 4 min., the Chelford and South Cave grains are equally coated with bond, and so

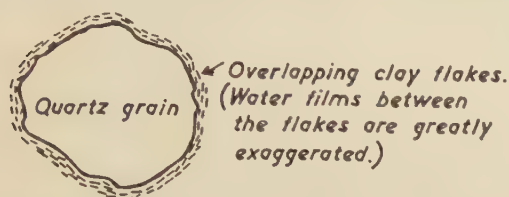


FIG. 28.—Ideal Distribution of Bond by Milling.

are indistinguishable (Fig. 11); the coating of the Chelford grains is rather more complete than that after milling for 2 min. No further change could be detected when the sample was milled for 20 min.

The structure of the bond covering the quartz grains after milling is shown diagrammatically in Fig. 28. Essentially, the structure is that of a series of overlapping flakes, arranged more or less parallel to the surface of the quartz grains. Each flake is an aggregate of structural units of the bonding minerals, stacked so that the units lie in parallel planes. As far as the bonding mechanism is concerned, each flake can be regarded as a single thick unit. Thus a flake of,

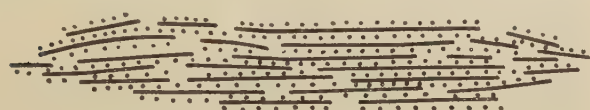


FIG. 29.—Diagrammatic Representation of the Structure of a Sericite Flake.

say, sericite acts as if it were a single unit carrying a negative charge sufficient to hold a number of cations at its surface; the structure of a sericite flake is suggested in Fig. 29. The bond enveloping a quartz grain is held in place by the surface tension of the water film over the outermost flakes, by the attractive forces between the flakes themselves, and by the attractive forces between the flakes and the quartz grains. The details of the bond structure vary according to the constitution of the minerals involved.

Three types of bond structure may be distinguished.

In the first type, the bonding minerals belong to the montmorillonite group or to the secondary-mica group. These minerals are characterized by the surface cations (the exchangeable cations). In the water film between two flakes, the water dipoles are interposed between the surface cations and the surfaces of the flakes, so that the positive charges on the dipoles are directed towards the flakes and the negative charges towards the cations. Thus between every pair of flakes there is the following sequence:

Clay flake with negative charge.
Oriented water dipoles.
Cations.
Oriented water dipoles.
Clay flakes with negative charge.

The cations occupy positions midway between the two flakes, and their charges are shared between the flakes. If the water dipoles are arranged in layers as suggested by Hendricks and Jefferson,⁴² then the layers will carry a positive charge on one face and a negative charge on the other; this structure is represented in Fig. 30(a). Alterna-

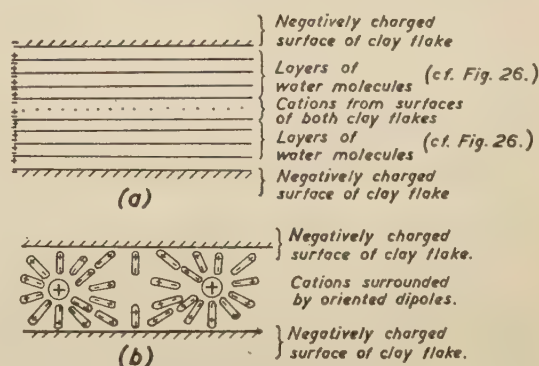


FIG. 30.—Structure of the Water Film between two Clay Flakes ((b) according to Marshall).

tively, the water dipoles may be arranged in chains, as was suggested by Marshall⁵⁸; his diagram of the structure of the water film is reproduced (Fig. 30(b)). As quartz has a negative surface charge the structure of the water film between a clay flake and a quartz grain resembles that of the water film between two clay flakes. There is one important difference; the cations are not so numerous, being derived from the clay flakes alone. Consequently the intensity of the electrostatic field between the quartz grains and the clay flake is not so high as that between two clay flakes. As a result, the clay flakes are not held so tightly to the quartz grains as to each other.

In the second type, the bonding minerals belong to the kaolin group. The structural units of these

minerals are held together in the flakes by the secondary attractive forces between the hydroxyl sheet of one unit and the oxygen sheet of the next. In each clay flake, one surface will be occupied by a more or less continuous hydroxyl sheet and the other by an oxygen sheet. The molecules in the water film between two flakes are oriented in accordance with these secondary forces, probably in sheets like those suggested by Hendricks and Jefferson. The structure of the film between a clay flake and a quartz grain will be similar to that between two flakes.

The cleavage of the limonite minerals into flakes does not occur so readily as in the clay minerals, owing to the greater attractive forces involved. The water film between two limonite flakes will probably be composed of sheets as in the kaolin minerals. As the limonite minerals have a positive surface charge and quartz a negative, there will be an intense electrostatic field between a limonite flake and a quartz grain, and the two will be held tightly together.

(3) *The Plasticity of Moulding Sands During Shaping.*

The shaping of moulding sand by ramming, squeezing, or jolting to form a mould or core involves a type of plastic deformation in which the sand is compacted while being deformed to the shape of the pattern or box. The bulk density is rarely uniform throughout the finished mould or core.

Thus it is frequently observed that, in hand-rammed moulds, the density of the sand adjoining the mould surface varies in a manner corresponding to successive additions of sand to the mould during ramming. The uppermost portion of each addition is denser than the lowermost one. The magnitude of the variation depends on the skill of the moulder.

Again, in machine moulding, it is generally agreed that hydraulic squeezing machines in which the sand is pushed round the pattern are not suitable for deep sections,⁴⁷ as there is too great a variation in density from the top to the bottom of the mould.

In the down-sand method of hydraulic squeezing, whereby the pattern is pushed into the sand, the sand adjoining the deepest part of the pattern has a higher density than that adjoining the shallowest part of the pattern.

In jolt-ramming, the density of the sand at any level in the moulding box is determined by the weight of the overlying sand. Consequently the sand at the bottom of the box is well compacted, while the density of that at the top is scarcely affected by the jolting and has to be compacted by hand-ramming or by mechanical squeezing.

(a) *Ideal Distribution of Bulk Density.*

The behaviour of the mould or core during casting is, in part, determined by this variation in density. Thus the portion of the mould with the greatest density will have the greatest resistance to the wash of the molten metal. Furthermore this portion of the mould will have the lowest permeability and will, therefore, be the most resistant to metal penetration of the mould surface. This variation in strength and permeability is illustrated by tests made on a green-sand mix from a local steel-foundry. The sand was made into test-pieces differing in bulk density; the relation of the green strength and of the permeability to the bulk density is shown in Fig. 31.

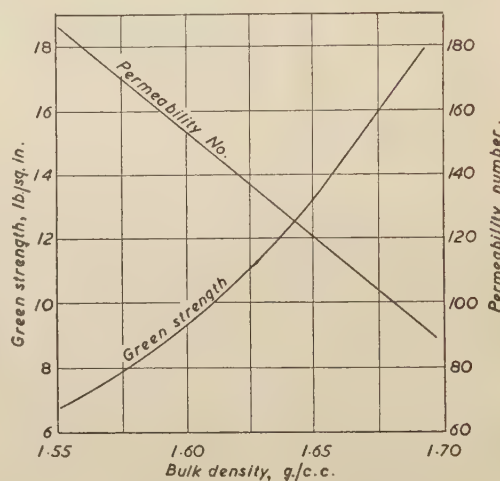


FIG. 31.—Green Strength and Permeability of a Green-Sand Mix.

At first sight it seems advantageous to ram the mould as tightly as possible. On the other hand tight ramming accentuates the fritting of the sand, and so may have an adverse effect on the finish of the casting. Furthermore, in green-sand practice the portions of the mould with low permeability may disintegrate as a consequence of the steam pressure developed during casting.

A certain range of variation of bulk density may be desirable in a mould or core. Thus in a green-sand mould the maximum density should be at the bottom of the mould, as there the ferrostatic pressure is greatest and the tendency for metal penetration of the mould surfaces is at its maximum. Higher up the mould the problem of escaping gases becomes increasingly important, hence a decrease in density upwards is desirable in order to prevent an increase in permeability. If the density at the bottom of the mould is sufficient to prevent metal penetration then, as the ferrostatic head decreases upwards, the density can be decreased upwards without increasing the tendency towards metal penetration.

This generalization requires modification in certain cases; for instance, the mould surface near the runner is subject to severe wash, consequently this part of the mould should be rammed to a high density so as to give the maximum resistance to wash.

(b) *Stress Distribution During the Shaping of a Mould.*

The preceding discussion emphasizes the importance of the bulk-density distribution. The mechanism underlying the distribution can be illustrated by reference to the shaping of a mould by squeezing. Stages in the squeezing are shown in section in Fig. 32.

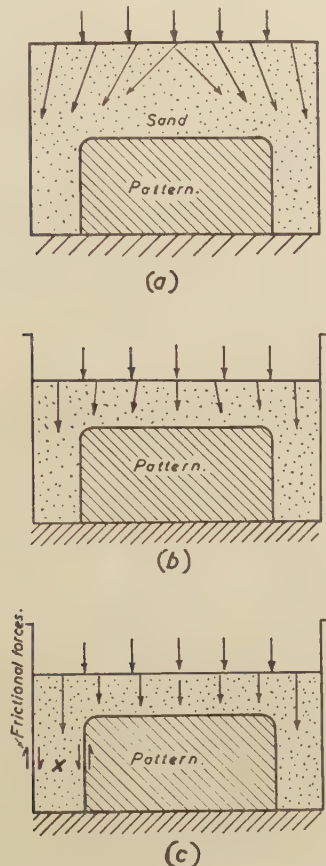


FIG. 32.—Compression of a Mould.

Initially, the box is filled with sand, aerated as is usual in foundry practice. In this condition, the sand has a bulk density of 0.60–0.75 g./c.c. As pressure is applied to the upper surface of the sand, flow takes place in the directions indicated by the arrows (Fig. 32(a)) so that part of the sand flows off the top of the pattern and down between the pattern and the box. The sand behaves as an incoherent system of particles. Redistribution of the sand in this manner tends to maintain a uniform bulk density throughout the mould.

For typical green-sand mixes, such redistribution takes place readily until a bulk density of roughly 1.50–1.55 g./c.c. is reached (Fig. 32(b)). Thereafter the sand behaves as a coherent aggregate. Continued application of the pressure increases the bulk density of the material directly above the pattern until an equilibrium is reached at which that pressure causes no further compression (Fig. 32(c)).

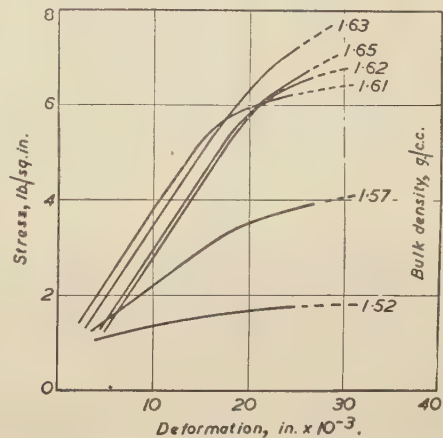


FIG. 33.—Deformation of Green-Sand Test-Pieces in Compression. (Owing to a small zero error in the machine, the curves do not pass through the origin.)

The difference in the moulding characteristics of the sand above and below the bulk density of about 1.50–1.55 g./c.c. can be demonstrated by reference to the stress/deformation curves of A.F.A. test-pieces subject to a slowly increasing compressive force. A representative series of

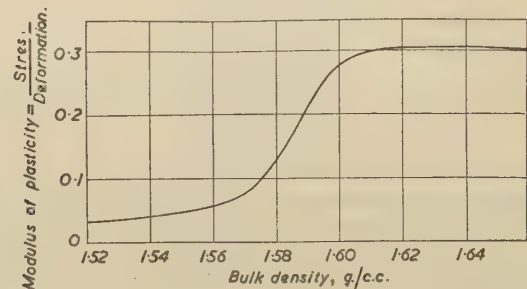


FIG. 34.—Deformation of Green-Sand Test-Pieces in Compression: Modulus of plasticity for straight portions of graphs plotted in Fig. 33.

curves for test-pieces prepared from the same mix but differing in bulk density is shown in Figs. 33 and 34. The curves indicate that for bulk densities above 1.61 g./c.c. for this mix, the force required to produce a given deformation is constant within the limits of experimental error. Below this bulk density, the force required decreases until, at 1.52 g./c.c., the force required is almost negligible; that is, below this bulk

density, the sand has little or no strength and its behaviour is that of an incoherent aggregate.

The Sand as an Incoherent Aggregate.—If the sand has been adequately milled, the clay bond will be evenly distributed over the grains. After milling, the flakes enclosing each grain are arranged parallel to the surface of the grain, and each flake is separated by water films from those adjacent. These clay-water envelopes enclosing the sand grains act as a lubricant between the grains. The bulk density of the aerated,* milled sand is determined by the thickness of these envelopes. In the experiments recorded below, the bulk density was determined by means of a 1000-c.c. glass measuring cylinder, 5.8 cm. in internal dia. and fitted with a grid level with the 1000-c.c. mark. The sand was aerated after milling by passing through a B.S.I. No. 5 sieve; 500 g. of the sand were poured through the grid into the cylinder as gently as possible. The grid determined the distance through which the sand dropped into the cylinder and ensured that concordant results were obtained by different operators.

The effect of moisture on the bulk density of an unbonded sand and on a bonded sand is illustrated in Fig. 35. It will be seen that, with increasing

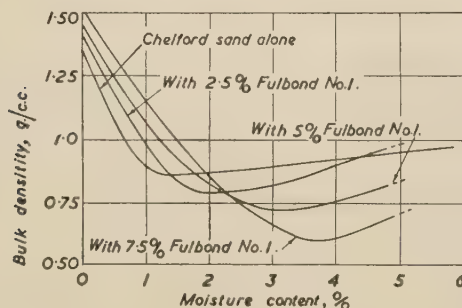


FIG. 35.—Effect of Bond Percentage on Bulk Density of Sand Mixes.

moisture content, the bulk density of the unbonded sand decreases until it reaches a minimum of 0.86 g./c.c. at 1.5% of moisture. When water is mixed with clean quartz grains, water layers probably develop on the surface of the grains in a manner akin to those on the surfaces of a clay flake. These layers are so firmly held in position by the negative surface charge on the quartz grains that, in effect, they increase the diameters of the grains. In the example, as the moisture content increases to 1.5%, more and more layers are added to the quartz grains, and the bulk density of the moist sand continues to decrease. If the moisture content is increased further, no additional water layers are formed around the quartz grains, as this added moisture is too far

from the surface charge of the quartz grains; instead, this added moisture forms a film of random-oriented molecules outside the water layers and is held in place by surface tension. When the sand grains are piled together, the film of random-oriented molecules outside the water layers is displaced, so that the water layers of one grain are in contact with the water layers of the next grain; the random-oriented molecules accumulate in the pores between the grains. In other words, the minimum bulk density is determined by the number of water layers which the quartz grain can hold firmly.

When the sand is placed in the measuring cylinder, the distance between the adjacent grains at any particular level is determined by the strength of the water film in relation to the weight of the overlying sand; near the bottom of the cylinder the grains will be closer together than at the top. The strength of the water film decreases outwards from the surface of the sand grain. Under the conditions in the cylinder there is, for each level in the cylinder, a limit to the thickness of the water film between adjacent grains; when this is attained, the moist sand reaches its minimum bulk density. When the moisture content is increased beyond 1.5%, the additional moisture fills the pores, and so increases the bulk density of the sand.

When a clay bond is present as well as moisture, the bulk-density/moisture curve for the sand mix is more sharply concave, and the minimum bulk density is less than that for the unbonded sand. This is because the clay-water envelopes around the sand grains developed by milling have a greater limiting thickness than that of water films alone, because of the stabilizing effect on the water layers of the charges on the clay flakes. Initially, the water films between the clay flakes are thin, and the water layers are so tightly held in place that it is difficult to displace the clay envelopes. If the mix is placed in a vessel without any shaking down, the quartz grains will be separated from each other by the clay envelopes, as suggested in Fig. 36(a). Only a few of the clay flakes in the envelopes are shown in the diagram, so as to emphasize the structure. As more and more moisture is added, the number of water layers between the clay flakes will increase to the stage at which they are still not easily displaced by the weight of the overlying grains. This stage is represented in Fig. 36(b); the number of flakes interposed between the quartz grains is the same. This is the condition for minimum bulk density. If the moisture content is increased still further, the layers are easily displaced by the weight of the overlying grains, so that fewer flakes are interposed between the quartz grains and the number of

* The aeration may be effected by passing the milled sand through a sieve or screen, so that aggregates formed by the milling are broken down to their constituent sand grains.

flakes in the pores increased. This structure is illustrated by Fig. 36(c); as the proportion of displaced flakes increases, the bulk density of the material will increase. In the example this corresponds to the stage beyond 5% of moisture.

pressure on the upper surface of the sand is transmitted through the sand in several ways. Part of the pressure is transmitted vertically through the sand to the top of the pattern and thence to the base-plate of the machine. The

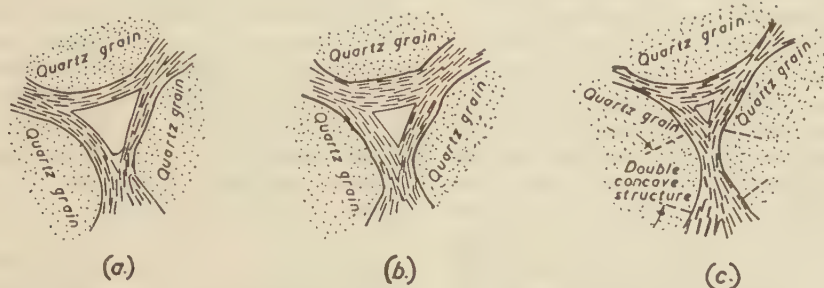


FIG. 36.—Bond Structure in Green Sand.

The measurement of the bulk density of the sand under the conditions already specified serves as an index of the strength of the clay-water envelopes, and so of their lubricating properties. A weak envelope will be displaced easily and allow the sand grains to come into direct contact, thus failing in its function as a lubricant. Ash and Lissell⁵⁹ have demonstrated a rather similar effect in connection with the ramming of A.F.A. test-pieces.

Experience has shown that if a moulding sand is tempered with varying amounts of water it will feel most plastic at the moisture content corresponding to the minimum bulk density. Other factors being equal, a sand which retains its plasticity over a wide range of moisture content is more useful than one whose plastic range is narrow; that is, of two sands giving the same minimum bulk density that yielding the less concave bulk-density/moisture curve is more useful than the one yielding the more concave curve. If the plastic range is wide, then drying off on the moulder's bench in the foundry is of less consequence than if the plastic range is narrow. The bulk-density/moisture curve for the ideal sand will thus be a shallow concave one like that for Fulbond No. 1 in Fig. 35.

Thus for the range over which the sand behaves as an incoherent aggregate its plastic properties may be deduced from its bulk-density/moisture curve, determined in the manner described above. The numerical values obtained for plotting the curve will vary according to the shape of the measuring cylinder. The one described is convenient and is readily obtainable.

The Sand as a Coherent Aggregate.—When the bulk density is high enough for the sand to have appreciable strength, the packing of the sand is seriously affected by frictional forces developed between the sand and the sides of the box and of the pattern. In Fig. 32 the

remainder of the pressure is transmitted to the sand between the pattern and the walls of the box.

This pressure is transmitted to the base-plate of the machine, in part directly through the sand and in part through the sides of the box and the vertical faces of the pattern by frictional forces. The pressure (pounds per square inch) on the sand at, say, x in Fig. 32 is less than the pressure (pounds per square inch) on the top of the sand, by an amount equal to the frictional forces between the overlying sand, the box, and the pattern.

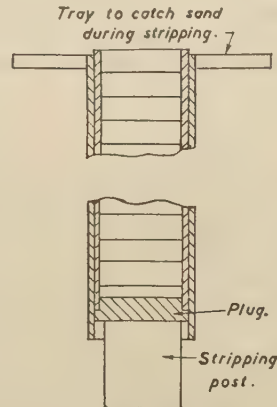


FIG. 37.—Apparatus for Comparison of Packing of Moulding Sands.

A series of experiments were made with the core-box shown in Fig. 37. This was designed so that the bulk density could be measured at intervals below the upper surface of a long cylindrical core prepared by squeezing under a pressure of 12.5 lb./sq. in. The core-box is composed of an inner tube divided into segments of equal thickness and machined so that it is a sliding fit in the outer tube. The lower end of the inner tube is closed by a plug. In operation, a known weight (400 g.) of the milled, moist

material is placed in the inner tube, after aeration; the surface of the sand is smoothed and a plunger inserted in the tube. A dead load of 28 lb. (equal to a pressure of 12.5 lb./sq. in.) is placed on the plunger and left on until no further consolidation of the material takes place. The load and plunger are then removed and the core stripped, one segment at a time; the weight of sand in each segment is determined to 0.1 g. As the segments have equal volumes (20 c.c.), the weight is a measure of the bulk density. From this data a curve can be plotted to show the bulk density at various depths below the top of the core; the slope of this curve for the top 5.0 cm. of the core is defined as the bulk-density gradient. It was found that for a core of 4.2-cm. dia., the sand more than 15 cm. below the surface was unaffected by the pressure on the top of the sand. In fact after the sand has once been compressed, the plug can be removed from the core-box and the sand in the lower part of the core-box will fall out, while sand in the upper part still sustains the pressure of 12.5 lb./sq. in. Differences observed in density distribution between two moulding-sand mixes also apply on the larger scale in foundry practice. Some of the factors governing the bulk-density gradient have been discussed elsewhere.⁴

(c) Graphical Representation of Plasticity.

Though the curve relating the bulk density of the aerated sand to its moisture content is of value in assessing the plastic range of the sand, it does not indicate the extent to which plastic

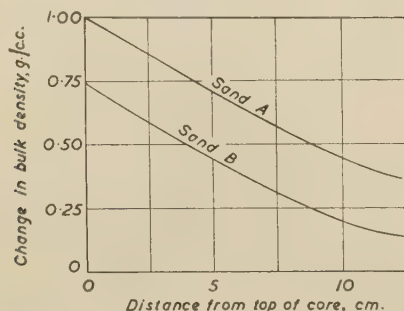


FIG. 38.—Graphical Representation of Plasticity.

deformation will take place in a sand subject to a given compressive force. This plastic deformation can be represented graphically by a modification of the graph indicating the bulk-density gradient. If, in the determination of the bulk-density gradient, the number of segments filled by the sand before squeezing is noted, the average bulk density of the sand can be calculated. Then, instead of plotting the bulk density after squeezing against the depth below the top of the core, the change in bulk density due to squeezing can be plotted. The bulk-density gradient is not affected

by this modification. The height of the graph above the horizontal axis is a measure of the plastic deformation. In Fig. 38 the graphs show that sand *A* undergoes a greater change of bulk density than sand *B*, and is therefore more plastic in the sense employed by Jeffreys.⁶¹

The modified graph indicates "ramability" which Ash and Lissell⁵⁹ define as "the ability of sand grains to move under pressure and form a compact body of uniform density". The height of the graph above the horizontal axis is a measure of the ability to move under pressure. The bulk-density gradient is a measure of the uniformity or otherwise of the density.

(d) Other Work on Plasticity of Sands.

The problem of comparing the plasticity or flowability of a moulding material has been approached by several workers. Kyle⁶² states: "Flowability, as applied to moulding sands, should indicate the property which permits sand to be rammed, squeezed, or jolted around a pattern in such a way that the energy applied causes the sand to surround the pattern completely and be at suitable, uniform hardness at the pattern surface without producing undesirable hardness conditions in other regions of the mould. Hardness was used in measuring this property because it is a simple test to make and, for any one sand condition, it can easily be correlated with the other sand properties which are of equal importance in a mould". He determined the hardness of the compacted material by means of the A.F.A. hardness meter; this is essentially a dial-gauge, arranged to measure the depth to which the plunger is forced into the material by the spring load in the gauge. The material was placed in a rectangular core-box of 12 in. \times 1 in. cross-section; the core-box was fitted with a removable side. After the sand had been compacted by ramming, jolting, or squeezing, the side of the core-box was removed, and the relative hardness was measured along the centre line of the exposed face, parallel to the direction of compression. By this means the variation in hardness with distance from the top of the core could be plotted, giving a curve the slope of which he defined as "the hardness gradient". From this curve he determined the percentage ratio of the average hardness of the core to its maximum hardness; this expression he defined as "the percentage flowability". The method can take no account of the bulk density of the material before compaction, though the hardness after compaction could no doubt be correlated with the bulk density, strength, &c., after the compaction. The importance of this change in bulk density has already been emphasized. A precise analysis of the factors involved in hardness has yet to be made. It depends not only on the bulk

density of the material, but also on its strength; a material with a low bulk density and high strength can have the same hardness as one with a high bulk density and low strength. This is because the hardness gauge measures the extent to which the material can be compacted by a given local pressure. A minor point is that the hardness gauge commonly employed is spring-loaded, consequently the load is not constant but depends on the depth of the indentation formed by the plunger.

In the "hardness-differential method" suggested by Kyle (*op. cit.*) test-pieces 2 in. in dia. and 2 in. long are rammed on the A.F.A. rammer, using a fall of $\frac{1}{4}$ in., instead of the usual 2-in. fall of the weight. Hardness readings are taken on top and bottom of the test-piece after each blow up to sixteen. The percentage flowability is defined as percentage ratio of the hardness at the bottom to that at the top of the test-piece. This method again raises the relationship of hardness to the other properties of a material.

In the sand-movement method of Dietert and Valtier,⁶³ the compaction of the sand between the fourth and fifth blows in the ramming of an A.F.A. test-piece (2-in. fall of weight) is measured by a dial-gauge. The percentage flowability is defined as:

$$100 - (100 \times \text{compaction in inches}).$$

The sand, after the blows of the rammer, has already reached a bulk density at which its strength is considerable, that is, the compaction is nearly complete. As in the other methods, no account is taken of the bulk density of the material before compaction.

Buchanan⁶⁴ emphasized the importance of bulk density, and has described a simple instrument for comparing the degree of ramming of a mould or core. It consists of a steel wire which is forced into the material by a falling weight. Apparently there is a straight-line relationship between the distance the wire penetrates into the material, and the bulk density. This method, like the others depending on hardness, cannot distinguish between variations in strength consequent on, say, moisture variations.

(4) *The Strength of Moulding Sands.*

The strength of a mould or core is of prime importance throughout its history; green strength, dry strength, hot strength, and residual strength have all to be considered.

Green Strength.—The strength of the moist sand after shaping must be sufficient for the mould to retain its shape during handling, and, in green-sand practice, it must also be sufficient to resist the wash of the molten metal during casting.

Dry Strength.—The strength after drying at a temperature of, say, 200° C. is of importance in

dry-sand practice, as it is a measure of the resistance to the wash of the molten metal. In all but the lightest green-sand castings, the mould becomes skin-dried before the wash of molten metal ceases, consequently dry strength is of importance in this respect.

Hot Strength.—The strength at high temperatures depends partly on the temperature and partly on the period for which that temperature is maintained; these depend on the weight of the casting. The mould for a heavy casting reaches a higher temperature in the vicinity of the runner than that for a light casting, and the molten metal washes over the mould surface for a longer period. Consequently the moulding sand used for a heavy casting must maintain its strength at higher temperatures and for a longer period than that used for a light casting.

Residual Strength.—The strength during the cooling of the casting is also of importance. After the casting has been poured, the strength of the moulding material usually decreases as cooling proceeds. If the strength falls off too rapidly, the casting will not receive sufficient support and may distort under its own weight. On the other hand, if the sand retains its strength too long, and is more or less surrounded by metal (*e.g.*, as in a core), it may resist the contraction of the metal to such an extent as to produce hot tears in the casting. When the casting is cool enough for the material to be knocked out of the box, the strength of the material should be low, to facilitate removal from the casting; this is of particular importance in connection with core sands, owing to the difficulty of fettling the interior of the casting.

(a) *Development of Bond Strength.*

In the milling test already described, the green and dry strengths of the mix were determined at various stages during the milling; the results are recorded in Fig. 39. The green strength increases in the early stages of milling but is almost constant after 3 min. The water films are then developed as extensively as possible in the bond and the bond is distributed as evenly as possible over the grains. The dry strength shows a similar increase in the early stages of milling and then becomes constant.

Daasch⁶⁵ has discussed the relation of the green strength of bentonite-sand mixes to their "mulling ratio"; the latter he defines as "the ratio of water by weight to clay content by weight, used in the milling of the mix". A series of mixes containing the same proportions of bentonite and sand were milled with different amounts of water, that is, the mulling ratio was varied. These mixes were dried and then all were tempered to the same moisture content—the tempering moisture content. Curves were then constructed to show

the relationship of green strength to mulling ratio for different tempering moisture contents. The peaks on these curves all occur at the same

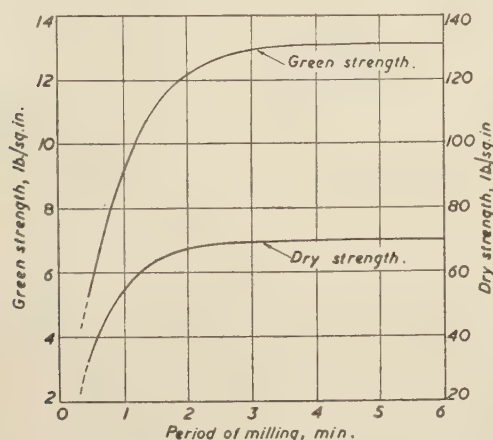


FIG. 39.—Development of Bond Strength by Milling.

mulling ratio; curves for one such series are shown in Fig. 40. If the green strength at this mulling ratio is plotted against the tempering

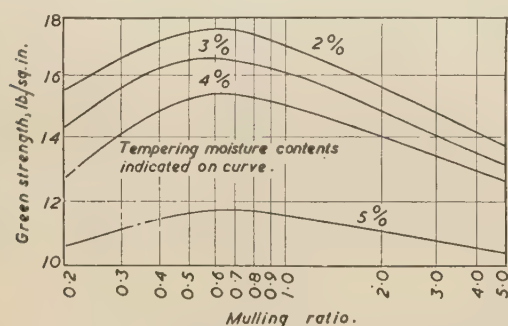


FIG. 40.—Green Strength in Relation to Mulling Ratio for a Sand Mix Containing 8% of Bentonite (according to Daasch).

moisture content, as in Fig. 41, it will be seen that the maximum green strength is obtained at a tempering moisture content much lower than that

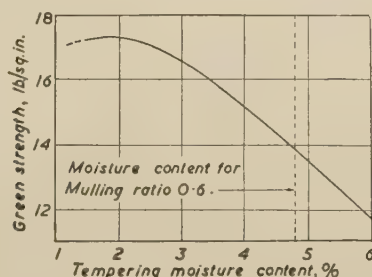


FIG. 41.—Green Strength of 8% of Bentonite Mix for the Mulling Ratio of 0.6%.

required for the mulling ratio. In other words, the most uniform distribution of bond and of the water films in the bond is obtained by milling at a

higher moisture content than that required for the maximum green strength. Daasch further showed that the maximum strength is obtained at almost the same mulling ratio as the maximum heat of wetting, that is, the maximum amount of heat evolved when water is added to the sand-clay mix.

(b) Bond Structure and Green Strength.

During the shaping of a mould or core from a moulding sand, the clay envelope around the quartz grains is partly displaced into the pores, so that the clay envelope between two quartz grains is double concave in section (see Fig. 36). The green strength of the sand depends partly on the extent to which this double-concave structure is developed and partly on the strength of the water films between the clay flakes and the quartz grains and between the clay flakes themselves.

Typical green-strength/moisture curves such as those shown in Fig. 42 have a peak form. At

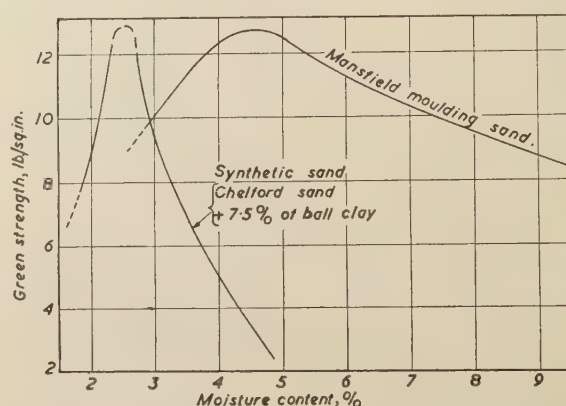


FIG. 42.—Green Strength of a Moulding Sand in Relation to its Moisture Content.

moisture contents below that of the maximum green strength, the water films are so thin and rigid that the double-concave structure does not develop readily; this structure is shown in diagrammatic form in Fig. 36(a). Beyond the maximum green strength, the double-concave structure develops readily but the rigidity of the water films is far lower; this structure is shown in Fig. 36(c). At the maximum green strength, there is just sufficient moisture to enable the double-concave structure to form satisfactorily while the water films are still fairly rigid; this structure is shown in Fig. 36(b). In other words, the maximum green strength is attained when a satisfactory balance has been reached between these opposing factors.

Creep in Green-Sand Moulds and Cores.—When the pattern is removed from the mould, the moulding material deforms under its own weight. The initial deformation is followed by "creep", that is, a further deformation with time. In a

series of tests on A.F.A. test-pieces composed of green sand, the "creep" was observed on the test-pieces at loads below that required to produce fracture. For loads less than 95% of the breaking load (measured under continually increasing load), creep was negligible after 2 min.; for loads greater than 95% the creep continued until, in many cases, fracture occurred. In other words, the breaking load measured when the test-piece is subject to a continuously increasing load is but slightly larger than that necessary to cause creep to failure. Thus the breaking load, under continuously increasing load, may be used as a measure of the strength in foundry practice.

(c) Bond Structure and Dry Strength.

The dry-strength/moisture curve for a synthetic sand is shown in Fig. 43. It will be seen that the

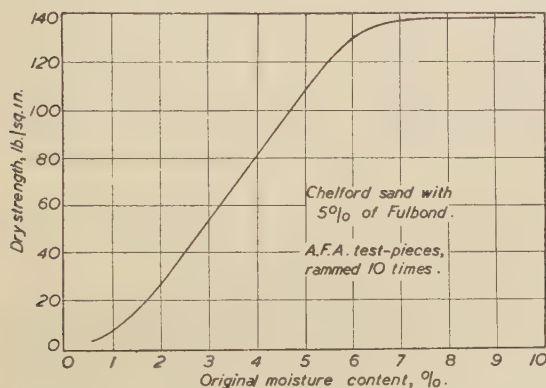


FIG. 43.—Dry Strength in Relation to Original Moisture Content before Drying at 200° C.

dry strength increases sharply as the moisture content (before drying) is increased, until a moisture content of 6% is reached. Above this moisture content the increase in dry strength is slight. Below 2% the dry strength is almost negligible because, in the green state, the double-concave bond structure already discussed is scarcely developed. As the moisture content is increased from 2 to 6%, the double-concave structure becomes more and more pronounced. Above 6%, the sand grains are as closely in contact as possible and the double-concave bond structure has attained its full development.

The cold dry strength decreases as the temperature of drying is increased above 200° C., provided that the test-piece is dried to constant weight. To illustrate this, the effect of drying temperature on the synthetic sand exemplified in Fig. 43 is shown in Fig. 44. The original moisture content was 3.5%. The test-pieces were crushed after they had been cooled in a desiccator to room temperature. It will be seen that the cold dry strength decreases from 22 lb./sq. in. for a drying temperature of 200° C. to nil for drying tempera-

tures of 700° C.; at the latter temperature the test-pieces fall to loose sand on cooling. The hot-dry-strength curve is also included in Fig. 44; in this case the test-pieces were crushed at the drying temperature, that is, there was no cooling.

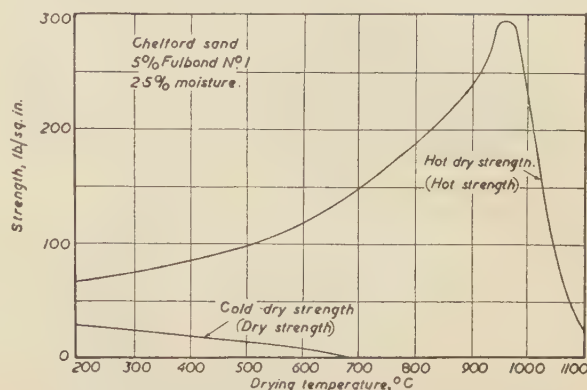


FIG. 44.—Hot and Cold Dry Strengths of a Synthetic Sand.

Within the temperature range 200–700° C., the hot dry strength (or hot strength) increases from 65 lb./sq. in. to 150 lb./sq. in. The decrease in strength on cooling is probably due to thermal shock consequent on the different coefficients of expansion of the bond and of the quartz; such shock is more marked as the drying temperature is increased. Thus in foundry practice it is desirable that dry-sand moulds should be closed and used as soon as possible after removal from the stove if the full advantage is to be obtained from the dry strength. If the moulds can not be used hot, it is preferable to dry them for a longer period at a lower temperature rather than for a shorter period at a higher temperature, as the thermal shock will then be minimized and the moulds will be equally well dried out.

(d) Bond Structure and Hot Strength.

In foundry practice it is the hot strength of a comparatively thin layer of moulding material at the mould surface that is of importance. When a test-piece of, say, B.C.I.R.A. dimensions is used to determine the hot strength of a moulding material, the thermal conductivity of the material affects the result. If a sand test-piece is heated at 800° C. for 5 min., the outermost $\frac{1}{8}$ -in. layer will be red-hot, while the interior may have only reached 200–300° C. Consequently it is necessary to heat for 10, or even 20 min. before the interior of the test-piece reaches a temperature approaching 800° C. During this interval the properties of the outer layers of the test-piece have also changed. Thus, even with a test-piece of this small diameter, only an approximate value of the hot strength can be obtained for correlation with the behaviour of the surface of a mould of the

same material when subject to the wash of molten metal for several minutes.

The hot-strength characteristics of a synthetic sand are shown in Fig. 45, where curves have been

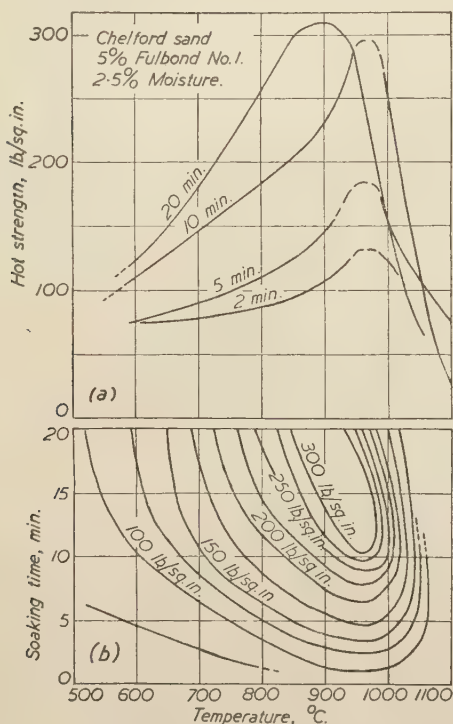


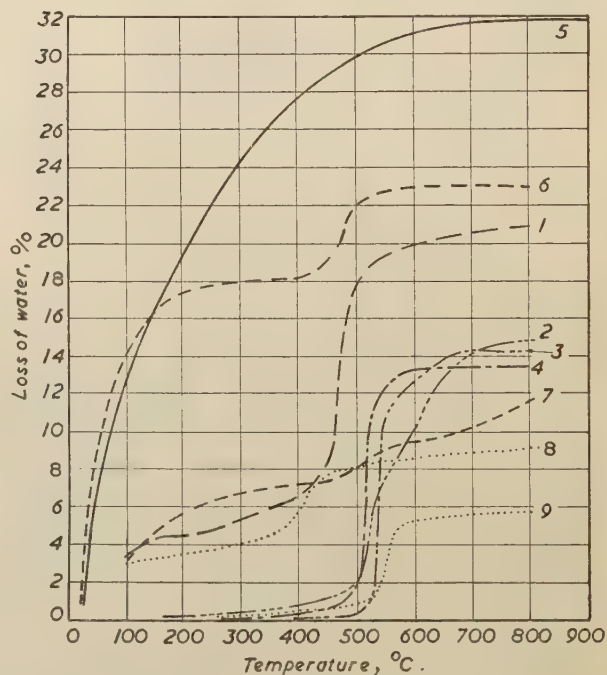
FIG. 45.—Hot-Strength Characteristics of a Synthetic Sand.

drawn for various periods of heating to show the relationship of hot strength to temperature. In all these curves the hot strength increases with temperature to a maximum value and then decreases sharply. Fig. 45(b), derived from Fig. 45(a), gives a better conception of the hot strength in relation to the temperature and the time of heating. In this graph the hot strength is plotted in the form of contours. The peak value of more than 300 lb./sq. in. is attained only for a limited range of temperature and time of heating. Ideally, a moulding sand should develop its maximum hot strength as quickly as possible, that is, the peak should be as near the temperature axis as possible, so that the maximum resistance to the wash of the molten metal is developed when it is most needed. The ideal relationship of the hot strength of the material to its temperature depends on the size of the casting for which the material is used. For a heavy casting the peak hot strength should be at as high a temperature as possible, in order to afford the maximum resistance to the wash of the molten metal.

The increase in hot strength (hot dry strength) from 200° C. to its maximum value at 950° C. has been illustrated in Fig. 44. The increase in

strength up to 600° C. is due to the gradual dehydration of the clay bond, that is, the reduction in the number of water layers between the flakes increases the rigidity of the bond structure. Obviously a point will be reached when the bond minerals will be completely dehydrated. As will be seen from the dehydration curves of the clay minerals, shown in Fig. 46, the minerals are completely dehydrated at about 600° C. The problem which then arises is that of the bonding mechanism above 600° C.

In the montmorillonite and secondary-mica groups, the work of Gruner⁶⁶ suggests that these clay minerals collapse to the talc or pyrophyllite structure after heating above 600–700° C. In the bond structure the flakes near an exposed surface will collapse fairly quickly on heating to, say, 750° C. Owing to their enclosed position, flakes deeper in the structure will have to be heated for a much longer period at 750° C., or for the same period at a higher temperature, before collapse is complete. In other words the complete collapse of these bonding minerals to the talc or pyrophyllite structure takes place over a range of temperature. When it is complete the bond will



Key.

1. Halloysite (Liège, Belgium).
 2. Nacrite (Brand, Saxony).
 3. Dickite (Mexico).
 4. Kaolinite (Ione, California).
 5. Allophane (Liège, Belgium).
 6. Montmorillonite (after Mehmel).
 7. Montmorillonite (after Nutting).
 8. Illite (Illinois, U.S.A.).
 9. Sericite (U.S.A.).
- } See reference 29.
} Quoted in reference 15.
} See reference 16.
} See reference 84.

FIG. 46.—Dehydration Curves of Clay Minerals.

have its maximum strength. Beyond this point the bond will begin to fuse and its strength will decrease rapidly.

In the kaolinite groups the work of Insley and Ewell⁶⁷ on kaolinite and dickite after heating to 600–900° C. showed that the material then gave no X-ray diffraction “pattern attributable to crystalline materials; the patterns all constituted of a broad diffuse band characteristic of amorphous materials”. This is in accord with the conclusions of Mellor and Scott⁶⁸ and Hyslop.⁶⁹

Fig. 47 shows that the effect of an increase in

is employed. From the moulder's standpoint, the sand should feel as plastic as possible; this condition is attained when the moisture content is that at which the sand attains its minimum bulk density before compression. For the sand with the moulding properties shown in Fig. 48, the moisture content for this condition would be 3.5%.

Reference to Fig. 48(b) shows that the moisture content mentioned is higher than that required for the maximum green strength. If the moisture content is reduced so as to increase the green

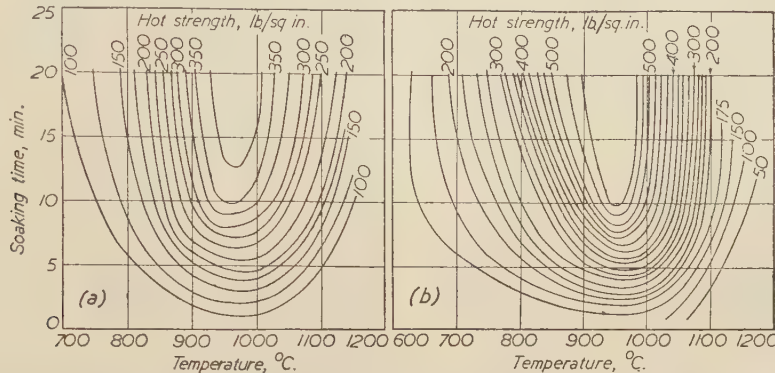


FIG. 47.—Hot-Strength Characteristics of Chelford Sand with 5% of Bentonite (a) at 2.5% and (b) at 5% of original moisture. B.C.I.R.A. test-pieces.

the original moisture content is to increase the peak hot strength without altering the temperature at which it is attained. The explanation lies in the better development of the double-concave bond structure with higher moisture contents, as in the case of dry strength.

(e) Bond Structure and Residual Strength.

Most of the synthetic sands prepared by bonding a high-silica sand with a clay, such as bentonite or fuller's earth, have little or no residual strength after they have cooled from temperatures above 600° C., unless the conditions have been severe enough to fuse the bond. Test-pieces heated to 600–1200° C. crumble to loose sand after cooling.

Naturally bonded sands and “compo”, on the other hand, may have considerable residual strength after cooling from 600–1200° C. to room temperature, although there may be no obvious signs of fritting. Belgian-yellow moulding sand, when close to the casting, bakes so hard that it sometimes has to be removed with a pick. This residual strength is mainly dependent on mechanical grading, provided that the bond has not fritted.

(5) The Moisture Content of Moulding Sands in Foundry Practice.

In green-sand practice several factors govern the moisture content at which the moulding sand

strength, the sand becomes more difficult to mould. If the moisture content is increased

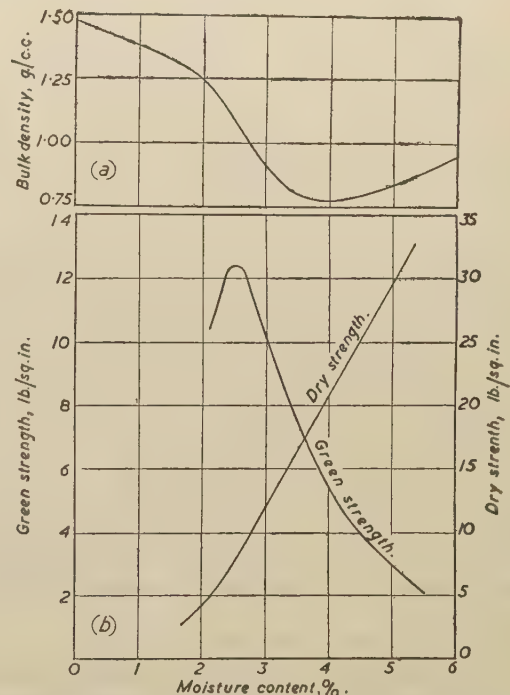


FIG. 48.—Moulding Properties of a Synthetic-Sand Mix. (a) Bulk density before compression; (b) green and dry strengths.

beyond 3.5%, the sand tends to adhere to the pattern (the "clagging" of the moulder) and the green strength is lowered unnecessarily. Furthermore the risk of blow-holes and associated defects is increased, owing to the greater amount of steam evolved.

In dry-sand practice the tendency is to increase the moisture content in order to obtain as high a dry strength as possible. There are obvious limits to this procedure. An increase in dry strength is obtained only up to a moisture content of 6% for the sand the properties of which are shown in Fig. 48; at this moisture content the green strength is too low for use in normal foundry practice. A further limit on moisture content is imposed by the drying capacity of the stoves. A balance must be struck between these opposing factors.

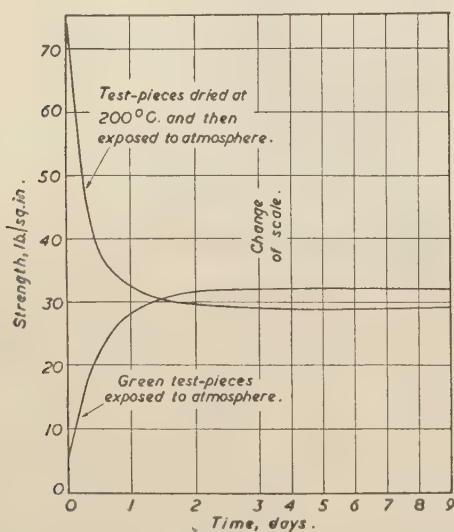


FIG. 49.—Effect of Atmospheric Exposure on Strength (Walker).

Walker⁷⁰ has shown that if green-sand test-pieces and dry-sand test-pieces are prepared from the same mix and allowed to stand exposed to the atmosphere for several days, the strength of both sets of test-pieces changes in the manner shown in the example (Fig. 49). The green-sand test-pieces increase in strength at first and then their strength becomes constant. The dry-sand test-pieces decrease in strength at first and then attain a constant strength. The final strengths of the green- and dry-sand test-pieces are almost equal. The final moisture content of the test-pieces, whether green or dry, is about the same (approximately 0.5%).

Thus clay-bonded moulds, whether green or dry, tend towards a constant moisture content, and consequently towards the same strength. This moisture content is an average value. In the green-sand test-pieces, the sand is driest at

the surface and dampest at the centre of the test-piece. In the dry-sand test-pieces the surface is moister than the centre. In both cases the surface layers of the test-pieces are green sands, the moisture contents of which are considerably lower than that required for the maximum green strength; in this moisture range the green strength is so low that the test-pieces have extremely friable surfaces. The same tendency is observed in green- and dry-sand moulds in foundry practice. It emphasizes the necessity of closing and pouring green-sand moulds as soon as they are shaped; dry-sand moulds should be cast into while still warm, to minimize the absorption of moisture from the atmosphere.

(6) The Refractoriness of the Sand.

The finish of the surface of a casting partly depends on the refractoriness of the moulding sand. If it is not sufficiently refractory, the sand will burn on to the casting and so cause trouble in fettling. Furthermore, if the grains frit together excessively, the residual strength of the mould or core will lead to difficulties in stripping.

The refractoriness of moulding materials may be compared by firing test-pieces of A.F.A. dimensions at 1550° C. for 2 hr. in a gas-fired furnace. Under these conditions, materials which are only refractory enough for iron casting fuse completely, whereas those suitable for steel castings show varying degrees of fritting.

There are some anomalies to be noted when relating the refractoriness of a material with the finish of a casting. For instance, some mild-steel castings were made in dry-sand moulds composed of a naturally bonded sand from Durham, together with a high-silica sand; this mix burnt on to half the surface of the casting. A rather less refractory naturally bonded sand was substituted for that originally used, and the area of burnt sand became almost negligible. This was because the latter mix formed a slaggy layer (less than 0.5 mm. thick) against the casting; this layer parted readily from the casting after cooling. The previous mix did not form a slaggy layer and burning-on occurred instead. Boswell² observed the same phenomenon with manganese-steel castings; the manganese reacted with the mould surface to form a film of slag.

Sarjant⁷¹ has described a sintering test based on the measurement of the temperature at which the sand grains at the surface of an A.F.A. test-piece just adhere to an electrically heated platinum strip. The sintering temperatures of a number of sands are given.

(7) The Permeability of Moulding Sands.

The permeability of moulding sands has been

discussed in the Second Report of the Moulding Materials Sub-Committee.*

IV.—THE CHARACTERISTICS OF TYPICAL BONDING CLAYS.

The bonding characteristics of clays are determined principally by the nature of their clay-mineral constituents; these characteristics may be modified by the presence of finely divided minerals such as quartz. Grim, Bray, and Bradley⁷² have given a preliminary account of the relationship of the strength and permeability of moulding-sand mixes to the clay-mineral constituents involved. This investigation was extended by Grim and Rowland.⁷³ Piper⁷⁴ has described the bonding properties of typical clays.

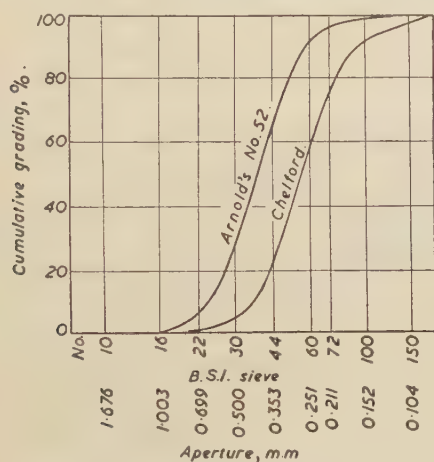


FIG. 50.—Cumulative Grading Curves for Arnold's No. 52 and Chelford Sands.

In the following pages, the bonding characteristics of clays which are being used in synthetic moulding sands (or which have been examined for this purpose) will be discussed in relation to their mineralogical constitution. To this end it is convenient to classify the bonding clays into three groups, depending on whether their dominant clay-mineral constituent belongs to the kaolin group, to the montmorillonite group, or to the secondary-mica group. Within each of these groups a further subdivision may be effected according to the mode of origin of the clay.

Certain bonding clays which have been tried in steel foundries are actually the clay-grade washings from crushed sandstones whose sand grade is required for use as a high-silica sand.

(1) Comparison of the Bonding Characteristics of Clays.

In order to compare the bonding characteristics of the clay, synthetic sands were prepared by

* *Journal of The Iron and Steel Institute*, 1942, No. II., pp. 393 P-454 P.

† First Report of the Moulding Materials Sub-Committee. *The Iron and Steel Institute*, 1938, *Special Report* No. 23, p. 141.

bonding a high-silica sand with one or the other of the clays. In their work, the Moulding Materials Sub-Committee† recommended the use of Arnold's No. 52 sand from Leighton Buzzard as the standard high-silica sand for this purpose. This sand was employed for some of the tests recorded in this section, but for the majority Chelford Sand was employed, as it is more sensitive to variations in the bonding characteristics. The mechanical gradings of the two sands are as follows :

	B.S.I. Sieves,	Arnold's No. 52 Sand, %.	Chelford Sand, %.
On No. 5	.	0.0	0.0
" 8	.	0.0	0.0
" 10	.	0.1	0.1
" 16	.	1.0	0.3
" 22	.	4.2	0.8
" 30	.	20.8	3.7
" 44	.	40.4	17.3
" 60	.	27.3	42.0
" 72	.	3.2	11.9
" 100	.	2.5	16.2
" 150	.	0.4	5.6
Through No. 150	.	0.1	2.3
		100.0	100.2

and their moulding characteristics are :

	Arnold's No. 52 Sand.	Chelford Sand.
Specific surface, sq. cm./g.	60.7	93.0
Average coefficient of angularity	1.05	1.08
Maximum packing density, g./c.c.	1.66	1.63

The cumulative grading curves are included in Fig. 50. It will be seen that both sands are well graded, and that Arnold's No. 52 sand is decidedly coarser than Chelford sand.

The majority of moulding-sand mixes employed in steel foundries have green strengths ranging from 6 to 12 lb./sq. in. In order to obtain comparable strengths it is generally necessary to employ about 7.5% of clays of either the kaolinite or the secondary-mica group, or 5.0% of clays of the montmorillonite group, with either Arnold's No. 52 sand or with Chelford sand. These proportions have been employed for most of the tests described in this section of the present paper.

(2) The Kaolin Group.

This group includes both residual and transported clays. The residual clays are represented by the china-clay deposits of Devon and Cornwall. The transported kaolin clays which are of value as bonds are usually associated with coal, lignite, or plant remains; they were transported by rivers and deposited in estuaries, lakes, and lagoons, that is, they accumulated in fresh or brackish

water. Clays of this type are represented by the Lower Tertiary ball clays of Devon and Dorset.

(a) China Clays.

The principal china-clay deposits at present being exploited occur in the Bodmin and St. Austell districts of Cornwall, and along the southern margin of Dartmoor. All three localities are situated on the outcrops of granite intrusions which have been decomposed by pneumatolysis⁵ (*loc. cit.*, p. 36). These granites were composed chiefly of quartz, orthoclase feldspar, and mica. The feldspar was decomposed by the action of steam and carbon dioxide, and, in its place, kaolinite appeared. As a result the granite was replaced by a soft mass of quartz, mica, and kaolinite.

contained more quartz than the $<10\mu$ fraction. The kaolinite in the $>10\mu$ fraction is in the form of vermicular aggregates, while that in the $<10\mu$ fraction occurs mainly as single flakes. In order to obtain a satisfactory X-ray diffraction pattern of the clay-mineral constituent, it was necessary to reduce the proportion of quartz by settling. The diffraction pattern showed that there is still an appreciable amount of quartz associated with the kaolinite. China-clay *B* is similar to china-clay *A*, but it contains a slightly higher proportion of quartz. Elutriation showed that 25% of the particles are less than 10μ across. The kaolinite is slightly coarser.

China-clay *C* differs from the other two kaolins in that it has been derived from an incompletely kaolinized granite. As a result, it contains 10–

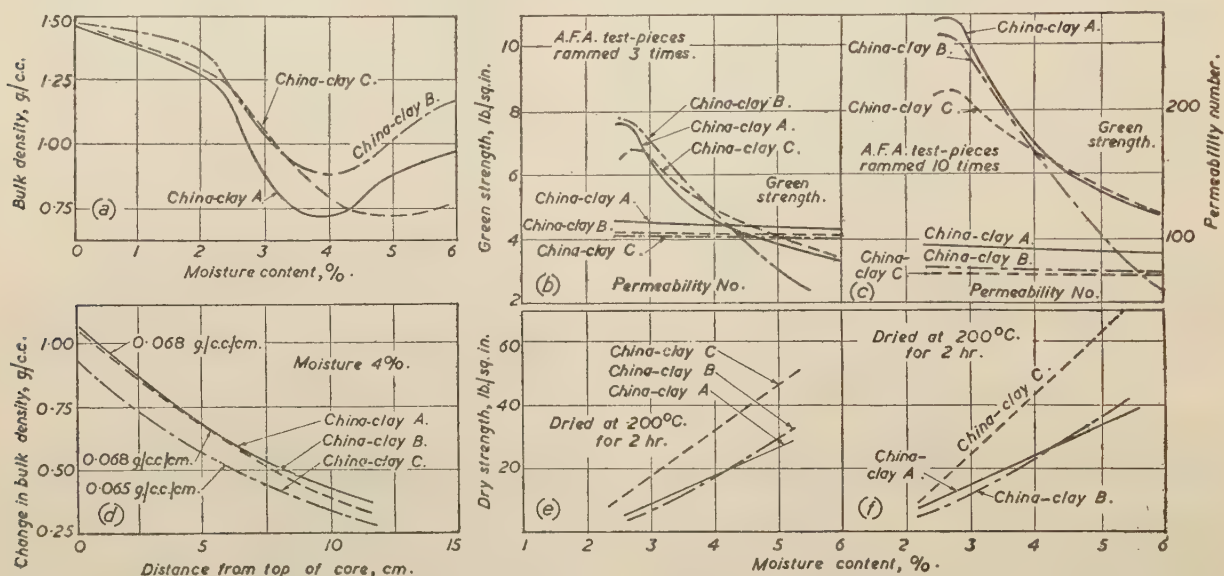


FIG. 51.—Bonding Characteristics of Typical China Clays. Chelford sand bonded with 7.5% of clay: (a) Bulk density before compression; (b) and (c) green strength and permeability; (d) bulk-density gradient; (e) and (f) dry strength (A.F.A. test-pieces rammed three and ten times, respectively).

China clay is composed essentially of kaolinite; quartz and mica are regarded as undesirable constituents. Consequently the winning of china clay is concerned principally with the separation of the kaolinite from the other constituents.

Commercial china clays vary in mineralogical constitution. They usually contain some finely divided quartz and muscovite mica, as the settling tanks do not effect a complete separation. Furthermore, if the kaolinization of the feldspar is not complete, secondary micas may be present as intermediate breakdown products. Three china clays, *A*, *B*, and *C*, were examined.

Petrography.—China-clay *A* is composed almost entirely of kaolinite; the other constituents are quartz, muscovite, and sericite. Elutriation showed that 30% of this clay is composed of particles less than 10μ across; the $>10\mu$ fraction

20% of secondary mica, as well as kaolinite, quartz, and muscovite. The secondary mica is of the sericite variety. Elutriation showed that 30% of the particles are less than 10μ across.

Bonding Characteristics.—The bonding characteristics of the three china clays are shown in Fig. 51. The curves for the bulk density before compression for china-clays *A* and *B* are similar in form; the minimum bulk density for china-clay *A* is considerably less than that for china-clay *B*. The bulk-density gradients for the topmost 5 cm. of the cores after compression are almost the same (0.071 g./c.c./cm.). The green strength of the china-clay *B* mix decreases rather more with increase in moisture content than that of the china-clay *A* mix. The dry-strength curves of the two mixes are practically identical. The permeability of the china-clay *A* mix

is slightly higher than that of the china-clay *B* mix.

The differences between the characteristics of these two kaolins are probably due mainly to the higher quartz content of china-clay *B* and, to a less extent, to its slightly coarser grain-size.

The china-clay *C* mix gives a minimum bulk density before compression as low as that given by the china-clay *A* mix; this density is attained at a rather higher moisture content. The bulk-density gradient for the topmost 5 cm. of the core is the same. The permeability of the china-clay *C* mix is about the same as that for the other kaolins and, like them, china-clay *C* is but slightly affected by the changes in the moisture content. It is in its strength characteristics that this kaolin

by rivers and deposited in estuaries or lakes. It was on the mudbanks that the swampy forests grew; this growing vegetation was responsible for various changes in the constitution of the upper layers of the mudbank. Thus the content of alkalis, lime, and magnesia was reduced either by solution due to the action of weak organic acids from the decaying vegetation in the swamp, or—particularly in the case of potash—by incorporation in the vegetation itself. These weak organic acids probably assisted in the segregation of the iron-bearing minerals in separate nodules or layers. Minerals containing ferrous iron, lime, magnesia, or the alkalis, lower the refractoriness of the underclay, hence the important part played by vegetation in the formation of refractory under-

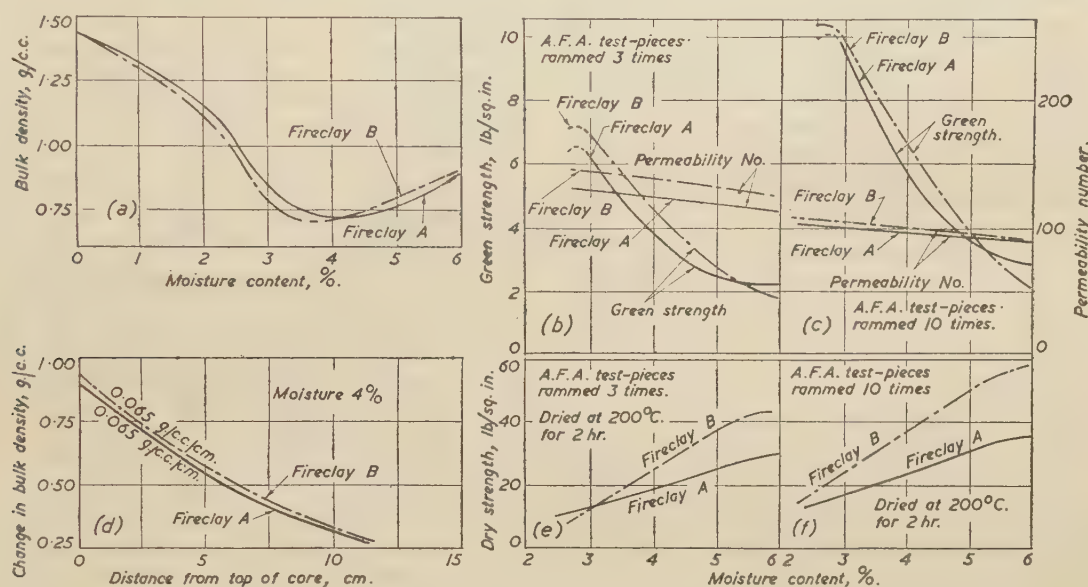


FIG. 52.—Bonding Characteristics of Typical Carboniferous Underclays. Chelford sand bonded with 7.5% of clay: (a) Bulk density before compression; (b) and (c) green strength and permeability; (d) bulk-density gradient; (e) and (f) dry strength.

differs so markedly from the other two. Its green strength decreases far less rapidly as the moisture content increases, while its dry strength is decidedly higher except at very low moisture contents.

(b) Carboniferous Underclays.

These clays are frequently known as fireclays, though strictly speaking this term should be limited to those underclays which are refractory. Underclays are worked in most of the British coalfield areas; details of their distribution are in a Geological Survey publication.⁷⁵

Each of these underclays represents the ancient soil or subsoil below a swampy forest, which may be preserved as a coal seam. Originally, mud or clay derived from the chemical weathering of older rocks on the adjacent land was transported

clays (*i.e.*, fireclays) will be appreciated. When this leaching of the underclay is complete, the resultant fireclay is usually composed of kaolinite, together with a variable proportion of finely divided quartz.

Though no doubt these underclays were originally quite as plastic as the clays of younger geological formations, they have been subject to greater changes, as a result of which they are now more indurated than the younger clays. Such hardened clays may again become plastic after prolonged exposure to the weather; the degree of plasticity attainable by weathering or by grinding is very variable, and the particles can rarely be made to attain the degree of dispersion observed in the younger plastic clays. Two typical fireclays, fireclay *A* and fireclay *B*, were examined.

Petrography.—Fireclay *A* is composed of

aggregates of kaolinite stained with limonite, together with finely divided quartz and a little secondary mica—about 5%. Elutriation showed that 40% of this clay is composed of particles less than 10μ across. The kaolinite aggregates are composed of flakes having random orientation. The secondary mica is principally sericite.

Fireclay *B* is similar to fireclay *A*, but it contains rather more sericite. Elutriation showed that 60% of this clay is composed of particles less than 10μ across.

X-ray diffraction patterns of the fine fractions of these clays show that kaolinite and quartz are

At all the localities, typical exposures of the beds show a series of flat-lying lenses of sandy clay, sand, and various grades of ball clay, interspersed with thin seams of lignite. The sand and clay were transported by rivers from the kaolinized granite intrusions of Devon and Cornwall and deposited separately; if the separation was incomplete, beds of sandy clay accumulated.

The characteristics of two typical ball clays, one from Devon and the other from Dorset, are described below.

Petrography.—The Devon ball clay examined is composed of kaolinite, together with a small

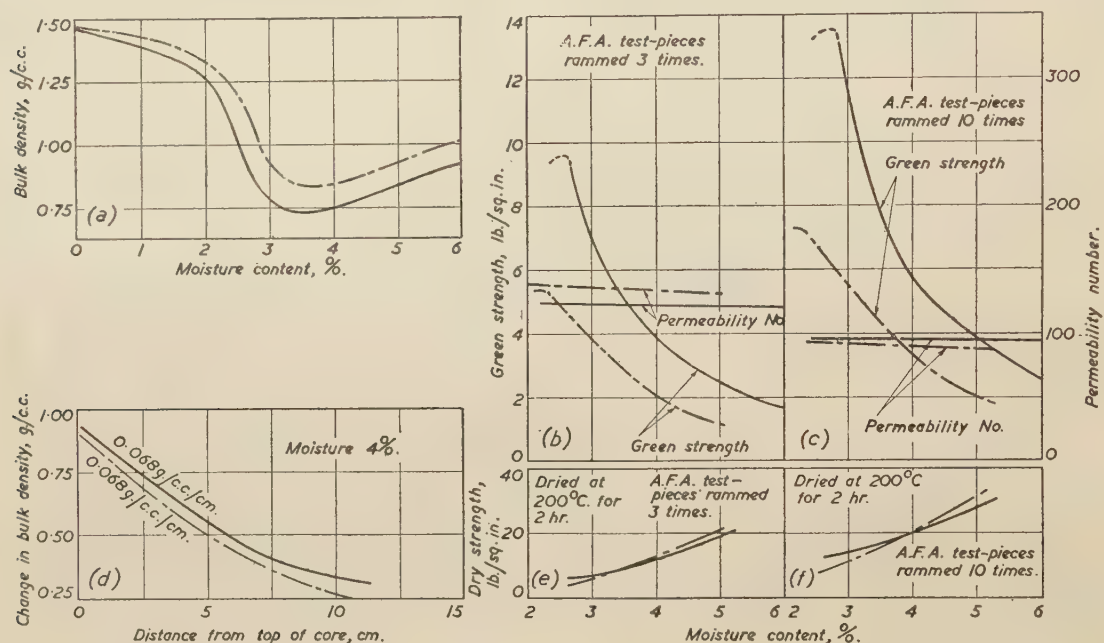


FIG. 53.—Bonding Characteristics of Typical Ball Clays. Chelford sand bonded with 7.5% of clay (1) Devon air-floated ball clay (continuous line) and (2) Dorset ball clay (broken line): (a) Bulk density before compression; (b) and (c) green strength and permeability; (d) bulk-density gradient; (e) and (f) dry strength.

the principal constituents of this fraction of both clays.

Bonding Characteristics.—The bonding characteristics of these two underclays are shown in Fig. 52. Comparison of the two sets of graphs shows that the only significant difference is in the dry strength. This difference is probably owing to the rather higher sericite content of fireclay *B*, and to its finer state of division.

(c) Ball Clays.

These clays are so called because the clay was formerly won by cutting it into cubes or "balls". Ball clays are worked near Wareham and Poole (Dorset), near Petrockstow (North Devon) and at Newton Abbot (South Devon). These clays are all of Tertiary age.⁷⁶

amount of quartz and a few flakes of sericite. The kaolinite is but slightly aggregated. Elutriation showed that 75% of the particles were less than 10μ across. The Dorset ball clay is similar to that from Devon, but it contains more quartz, and the kaolinite forms larger aggregates. Elutriation showed that 60% of the particles were less than 10μ across.

X-ray diffraction patterns of the fine fraction of the two clays showed that the quartz lines in the Dorset-clay pattern are stronger than those in the Devon-clay pattern.

Bonding Characteristics.—The bonding characteristics of these two ball clays are shown in Fig. 53. There is little difference between them. The Devon clay has a lower minimum bulk density before squeezing than has the Dorset clay; this

difference is probably owing to the higher quartz content of the latter.

(3) *The Montmorillonite Group.*

The montmorillonite minerals are the essential constituents of bentonite and fuller's earth, and also occur in certain of the younger marine clays. At present only bentonite and fuller's earth are extensively employed as bonds.

(a) *Bentonite.*

Hewitt⁷⁷ and Wherry⁷⁸ have assembled data showing that bentonite is leached and hydrated volcanic ash, while Kerr⁷⁹ has suggested that the fuller's-earth bed in the Woburn Sands of Bedfordshire is an altered volcanic ash. In both cases the original material was dust and ash (*i.e.*, pulverized glassy lava) blown out from volcanoes; this debris included shards of volcanic glass. Tomlinson and Meier⁸⁰ have described an occurrence of montmorillonite in which the various stages in the decomposition of albite-oligoclase feldspar (sodaplagioclase) to montmorillonite can be traced; they and other workers have emphasized the important part played by magnesium in this change. Hauser and Reynolds⁸¹ have confirmed this experimentally.

The principal commercial deposits of bentonite are found in South Dakota, Wyoming, and California, though there are deposits of varying size in Tennessee, Texas, Arizona, and in Western Canada; bentonites also occur in Algeria and New Zealand. Each bed of bentonite records the explosion of a volcano which ejected a vast body of pulverized glassy lava into the atmosphere; this air-borne debris was carried off by the winds and gradually settled on the earth's surface. This layer of ash is thick in the vicinity of the volcano and gradually becomes thinner as the distance from the volcano increases. Thus the Tennessee deposits extend over an elliptical area about 800 miles long by 450 miles wide. The scale of the volcanic explosions which resulted in the formation of deposits of this kind may well be compared with that at Tamboro, near Java, in 1815. About 35 cu. miles of material were blown into the air; so thick was this cloud of material that it caused darkness for three consecutive days over a distance of up to 300 miles from the volcano. The dust was deposited over an area of 1,000,000 square miles. In the case of the South Dakota and Wyoming deposits,⁸² the volcanoes responsible were probably in the Middle Rocky Mountains. Where this pyroclastic material accumulated in a moist climate, decomposition occurred and a bentonite deposit was formed.

(b) *Fuller's Earth.*

The principal British fuller's earth deposits worked are at Combe Hay (near Bath), at Redhill

(Surrey), and at Woburn (Bedfordshire).⁹ Like the bentonite deposits of North America, they were probably formed from volcanic ash, but, unlike them, they do not extend over great areas. For instance, the fuller's-earth beds in Surrey have a maximum thickness of 48 ft. at Nutfield and extend over a distance of 6 miles from east to west, that is, the beds have a lenticular form. The same is true of the Somerset and the Bedfordshire deposits. The Surrey and the Bedfordshire deposits are of Cretaceous age, while those of Somerset are of Jurassic age. Newton⁹ considers that the fuller's earth accumulated in much the same way as sand, mudbanks, and shoals accumulate in estuaries at the present day. Consequently, the fuller's-earth beds are not found extending over wide areas. The source of the volcanic ash in these fuller's-earth beds is still obscure.

The characteristics of three clays of this group are described here; their sources are as follows:

Bentonite: Wyoming, U.S.A.

Fulbond No. 1 } Two types of fuller's earth, supplied
Fulbond No. 3 } by the Fullers' Earth Union, Ltd.

Petrography.—The Wyoming bentonite is mainly composed of sodium montmorillonite, together with a small amount of quartz. The montmorillonite forms aggregates which break down in water to form flakes, for the most part less than 1μ across.

The fuller's earths are composed of calcium montmorillonite and calcite, together with a small amount of quartz and anorthoclase.^{83,9} The montmorillonite forms aggregates most of whose constituent flakes are less than 1μ across. Fulbond No. 1 is essentially powdered fuller's earth. Fulbond No. 3 is powdered fuller's earth to which a small proportion of sodium carbonate has been added; in the presence of moisture, base-exchange occurs whereby calcium montmorillonite is converted to sodium montmorillonite.

X-ray diffraction patterns for Fulbond No. 1 show conspicuous calcite lines, although the amount of calcite is far less than that of montmorillonite.

Bonding Characteristics.—The bonding characteristics of the three clays are shown in Fig. 54. The comparison drawn between them is of particular interest because it demonstrates the important part played by the exchangeable cation in these clays. Fulbond No. 1 illustrates the bonding characteristics of calcium montmorillonite, while Fulbond No. 3 and Wyoming bentonite illustrate the bonding characteristics of sodium montmorillonite. The Fulbonds have a rather lower montmorillonite content than Wyoming bentonite and thus are not quite so efficient as bonds.

The curve for the bulk density before squeezing for the Fulbond No. 1 mix is more concave than

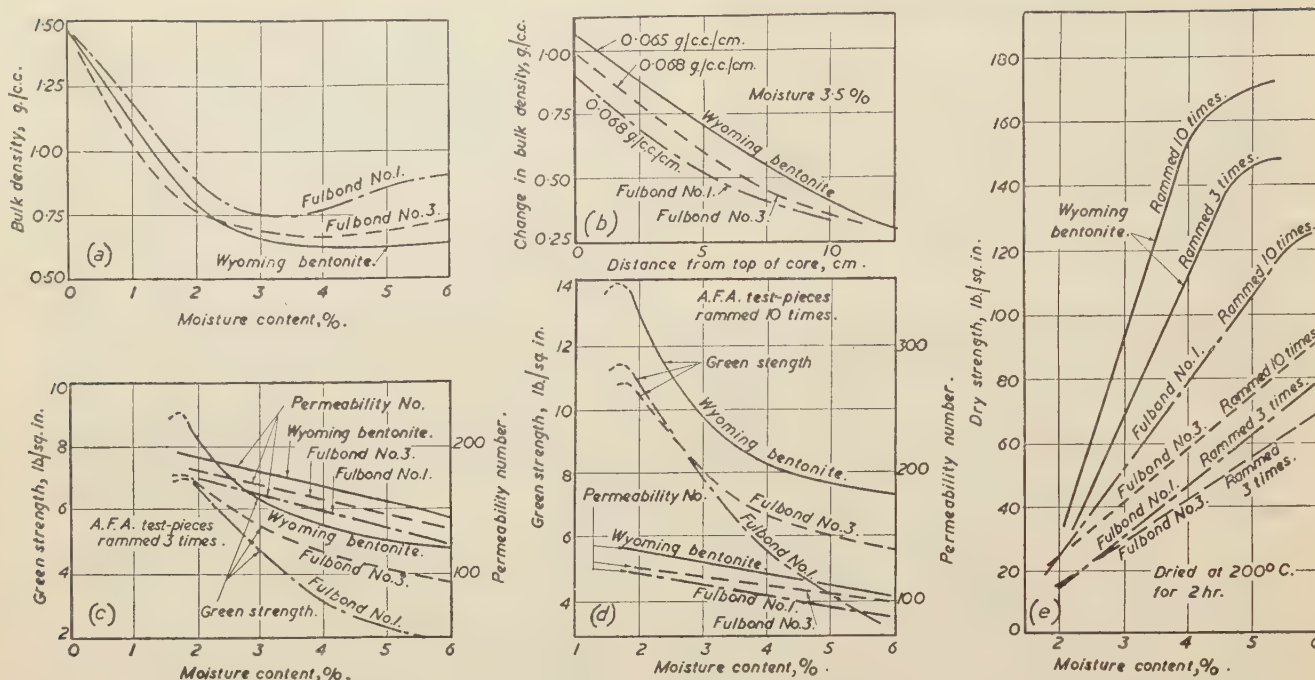


FIG. 54.—Bonding Characteristics of Bentonite and Fuller's Earth. Chelford sand bonded with 5.0% of clay : (a) Bulk density before compression; (b) bulk-density gradient; (c) and (d) green strength and permeability; (e) dry strength (A.F.A. test-pieces).

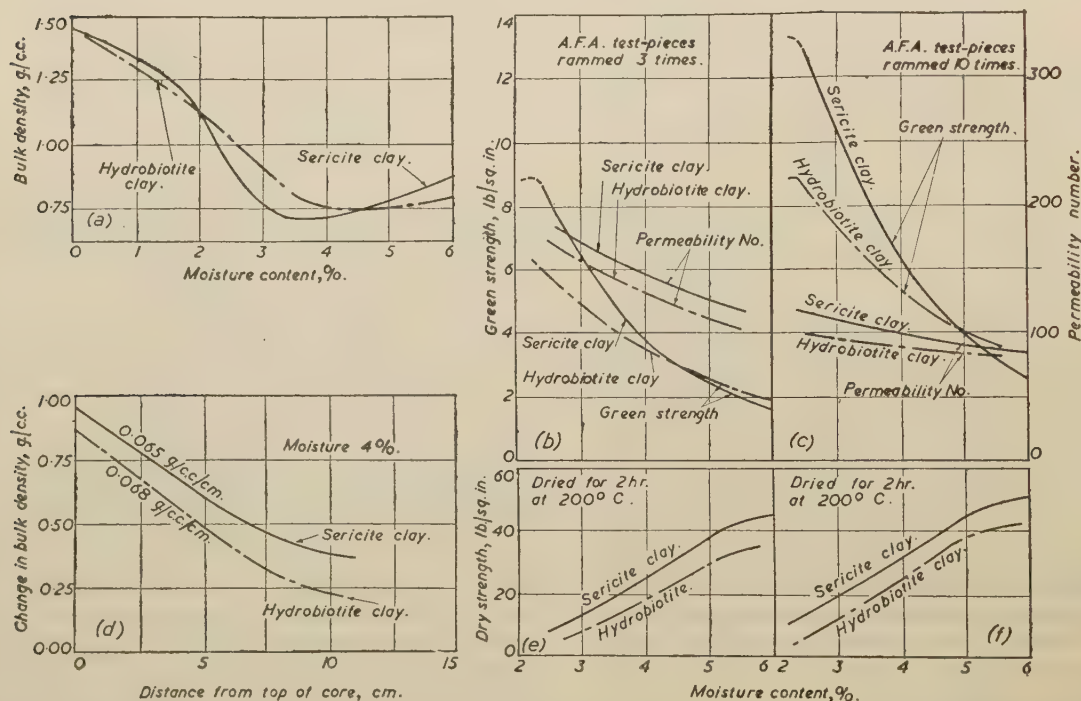


FIG. 55.—Bonding Characteristics of the Secondary-Mica Clays. Chelford sand bonded with 7.5% of clay : (a) Bulk density before compression; (b) and (c) green strength and permeability; (d) bulk-density gradient; (e) and (f) dry strength (A.F.A. test-pieces rammed three and ten times, respectively).

those for the Fulbond No. 3 and bentonite mixes, that is, the bulk density of the Fulbond No. 1 mix is rather more sensitive to changes in moisture content. The bulk-density gradients for the top-most 5 cm. of the cores are practically the same for all three mixes.

The permeability of all three mixes decreases considerably as their moisture content increases. This is because montmorillonite swells considerably in the presence of water and tends to fill the pores.

The green-strength curves for bentonite and Fulbond No. 3 are similar in form, but for a given moisture content the bentonite mix is appreciably stronger, mainly because of its higher montmorillonite content. As the moisture content increases, the green strength of these two mixes

teristics of the two clays are shown in Fig. 55. It will be seen that the curve for the bulk density before compression for the sericite clay is more sharply concave than that for the hydrobiotite clay, that is, the sericite clay has not such a wide plastic range as the hydrobiotite clay. The bulk-density gradients are nearly equal.

The green-strength/moisture curves for the sericite clay are steeper than those for the hydrobiotite clay. The maximum green strength of the sericite clay is higher than that of the hydrobiotite; this is due, at least in part, to the larger amount of quartz in the latter. The permeability of both mixes shows a marked decrease as the moisture content is increased. The dry strength of the sericite clay is slightly higher than that of

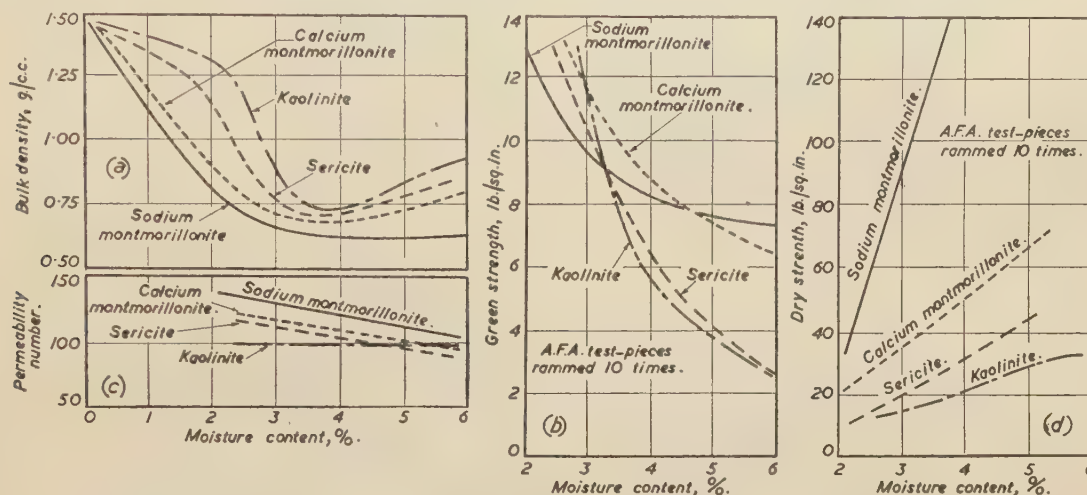


FIG. 56.—Bonding Characteristics of the Clay Minerals. Chelford sand bonded with 5.0% of montmorillonite clay, or with 7.5% of sericite or of kaolinite clay: (a) Bulk density before compression; (b) green strength; (c) permeability; (d) dry strength.

decreases more slowly than that of the Fulbond No. 1 mix.

The dry-strength curves for bentonite are decidedly steeper than those for the Fulbonds. There is less difference between those of the two Fulbonds.

(4) The Secondary-Mica Group.

These micas are the essential constituents of most indurated argillaceous sediments and form the bond of many sands and friable sandstones used for moulding.

The characteristics of two clays, rich in sericite and hydrobiotite respectively, are described here. The sericite clay contains, besides sericite, a small proportion of quartz; the hydrobiotite clay contains more quartz than does the sericite clay. Elutriation showed that in the sericite clay 65% of the particles were less than 10μ across, while in the hydrobiotite clay 60% of the particles were less than 10μ across.

Bonding Characteristics.—The bonding charac-

teristics of the two clays are shown in Fig. 55. It will be seen that the curve for the bulk density before compression for the sericite clay is more sharply concave than that for the hydrobiotite clay, that is, the sericite clay has not such a wide plastic range as the hydrobiotite clay. The bulk-density gradients are nearly equal.

(5) Bonding Characteristics in Relation to Mineralogical Constitution.

From a comparison of the bonding characteristics of these clays, the bonding characteristics of some of the different clay minerals can be deduced. Curves derived in this manner are shown in Fig. 56. From these graphs it will be seen that there are marked differences between the behaviour of the several clay minerals. A curve for hydrobiotite was not included, as a reasonably pure sample could not be obtained; however, all the evidence available suggests that its characteristics are intermediate between those of sericite and calcium montmorillonite.

(a) Bulk Density before Compression.

The curve for kaolinite is more sharply concave than the other curves, that is, kaolinite has the shortest plastic range of these clay minerals. The

plastic range increases from that of kaolinite in the order sericite, calcium montmorillonite, and finally sodium montmorillonite.

(b) *Bulk-Density Gradient.*

The bulk-density gradient appears to be almost independent of the nature of the clay bond, for all the values lie between 0.068 ± 0.003 g./c.c., that is, a range within the margin of experimental error.

(c) *Permeability.*

The permeability of mixes bonded with kaolinite shows little change as the moisture content is increased. Sericite- and montmorillonite-bonded

rapid for sodium montmorillonite and progressively less rapid for calcium montmorillonite, sericite, and kaolinite.

(f) *Hot Strength.*

This has been discussed in a separate paper.⁶⁰

(6) *Bonding Characteristics in Relation to the Base Sand.*

Though the conclusions drawn above are based on mixes in which Chelford sand forms the base, they are independent of the base sand and therefore are of general application. For instance, the bonding characteristics of Fulbond No. 1 and

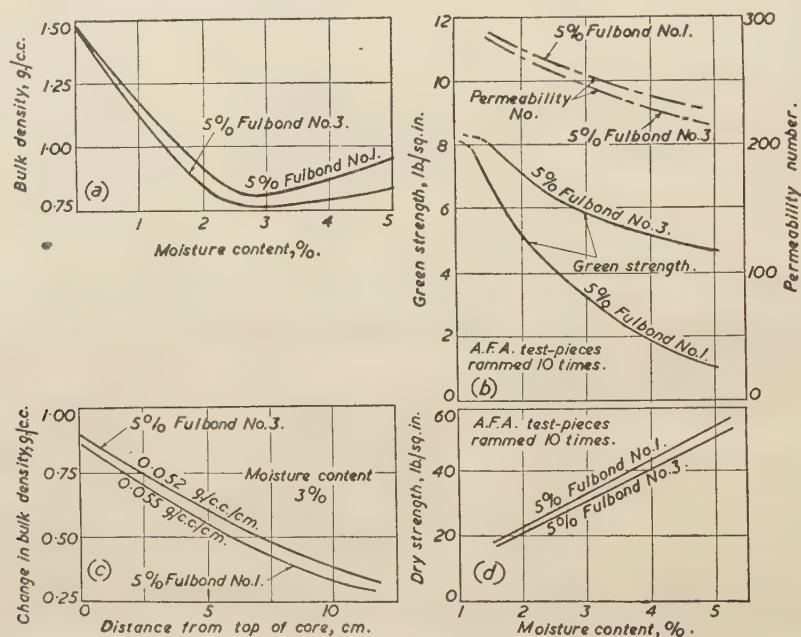


FIG. 57.—Bonding Characteristics of Fulbond Nos. 1 and 3 with Arnold's No. 52 Sand: (a) Bulk density before compression; (b) green strength and permeability; (c) bulk-density gradient; (d) dry strength.

mixes, on the other hand, show a marked decrease in permeability as the moisture content is increased.

(d) *Green Strength.*

Two features are shown by these graphs. Firstly, that in order to obtain roughly comparable green strengths, 7.5% of kaolinite and sericite are necessary instead of 5.0% as is the case with montmorillonite. Secondly, the rate of decrease of green strength as the moisture content is increased is most rapid for kaolinite and progressively less rapid for sericite, calcium montmorillonite, and finally sodium montmorillonite; that is, kaolinite mixes are the most sensitive to moisture variation and sodium montmorillonite mixes the least sensitive.

(e) *Dry Strength.*

The rate of increase of dry strength, as the original moisture content is increased, is most

Fulbond No. 3 with Arnold's No. 52 sand are shown in Fig. 57. They differ from those obtained with Chelford sand (Fig. 54) in the actual values of the several characteristics; thus the green strengths of the Arnold's mixes are lower than those of the Chelford mixes. With both sands, however, the green-strength/moisture curve for Fulbond No. 1 is much steeper than that for Fulbond No. 3, and the curve for the bulk density before compression for Fulbond No. 1 is more sharply concave than that for Fulbond No. 3.

(7) *Bonding Characteristics in Relation to the Proportion of Bond.*

The effect of the proportion of bond on the bonding characteristics is illustrated by Fig. 58, showing the characteristics of Chelford sand with different proportions of a ball clay. Comparisons of the graphs show that:

(i) Both curves for the bulk density before compression are sharply concave. The minimum bulk density is rather lower with 7.5% of clay than with 5.0% of clay, and it occurs at a rather higher moisture content.

(ii) The bulk-density gradient is the same for 5.0% and 7.5% of clay, but the change in bulk density at any level in the core-box is less for 5.0% of clay than for 7.5% of clay.

(iii) Both the green-strength/moisture curves are steep, but, for a given moisture content, the green strength for 5.0% of clay is much lower than that for 7.5% of clay.

clay-mineral structure. The water films between the flakes in kaolinite clays are stabilized by weak secondary forces existing between the hydroxyl sheet of one structural unit and the oxygen sheet of the adjacent unit. The water films in the montmorillonite and secondary-mica clays are more firmly held than in the kaolinite clays, by virtue of the stronger electrostatic field existing between the cations and the excess charges on the structural units. The field is stronger in the secondary micas than in the montmorillonites, consequently water films do not enter between the units in the secondary-mica clays as readily as

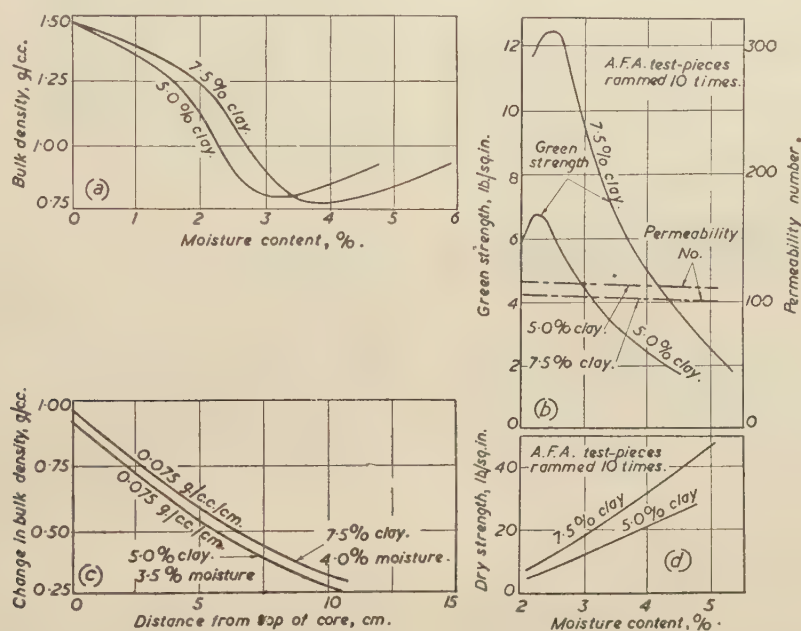


FIG. 58.—Moulding Characteristics of Chelford Sand bonded with Ball Clay: (a) Bulk density before compression; (b) green strength and permeability; (c) bulk-density gradient; (d) dry strength.

(iv) The permeability number for 5.0% of clay is rather higher than that for 7.5% of clay.

(v) The dry strength for 7.5% of clay increases more rapidly with moisture content than for 5.0% of clay.

(8) Bond Structure in Relation to Bonding Characteristics.

The ball clay employed in the tests the results of which are illustrated in Fig. 58 was composed of kaolinite, together with a very small proportion of sericite and practically no quartz. Comparison of the 5.0% curves for this clay with those for Chelford sand with 5% of Fulbond, or with Wyoming bentonite (Fig. 54) show that at this proportion of bond the green and dry strengths of the ball clay are inferior to those of Fulbond or bentonite and that the curve for the bulk density before compression is more sharply concave for ball clay than for the other two clays. These differences are consequent on the differences in

they do in the montmorillonite clays, hence the structure of overlapping flakes is not so finely developed in the former as in the latter. In the montmorillonite clays, the extent to which water films enter between the units depends on the nature of the exchangeable cation. In calcium montmorillonite the charges in the sheets of exchangeable cations between the units are more localized than in sodium montmorillonite, owing to the different valencies of the cations, which means that in the cation sheets in calcium montmorillonite there are only half the number of ions as compared with the cation sheet in sodium montmorillonite, though the calcium ions carry twice the charge. At low moisture contents, the water films in calcium montmorillonite are more firmly held than those in sodium montmorillonite, because of these more localized electrostatic fields, so that the green strength of calcium montmorillonite is higher than that of sodium montmorillonite. As the moisture content is increased,

the green strength of calcium montmorillonite (see Fig. 56) decreases more sharply than that of the sodium montmorillonite, because the less uniform calcium cation sheets are not so effective in maintaining the stability of the water layers as are the more uniform calcium cation sheets.

The bonding characteristics in the green state are ultimately a function of two opposing factors, *viz.*, the ability of water to enter between the structural units of the clay minerals, and the stability of the water layers which have entered; the clay minerals can be grouped according to the relative importance of these two factors, as follows :

	Entry of Water Films.	Strength of Field Stabilizing the Water Films.
Kaolinite	Very easy.	Low.
Sodium montmorillonite . .	Easy.	Moderate.
Calcium montmorillonite . .	Moderate.	Strong, but localized.
Secondary mica	Difficult.	Strong.

Thus the ideal in the green state is that the water films should enter easily and be stable after entry; in practice a balance must be struck between the two factors.

(9) *The Rate of Development of Green Strength.*

The rate at which the green strength of a sand mix is developed depends mainly on the specific surface of the dry clay as it is added to the sand,

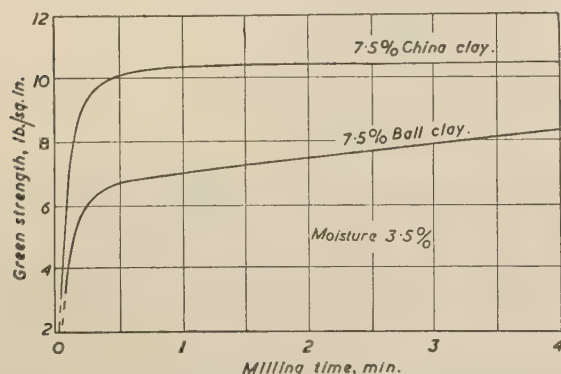


FIG. 59.—Rate of Development of Green Strength. Chelford sand.

and on the ability of the water films to enter between the structural units. For instance, Fig. 59 shows the rate of development of green strength for two clays, mineralogically similar but whose specific surfaces in the dry state differ considerably. The specific surfaces are :

China clay	13,300 sq. cm./g.
Ball clay	6,000 "

The green strength of both clays increases sharply in the early stages of milling. After

milling for 1 min., the green strength of the china-clay mix is constant, but that of the ball-clay mix continues to increase as the milling breaks down the ball-clay aggregates. In the tests recorded earlier in this section, the mixes were milled until the strength was fully developed.

V.—CONCLUSIONS.

The fundamental characteristics of moulding sands can be assessed on a geological basis. Moulding sands, whether synthetic or naturally bonded, should be composed of two grades only, *viz.*, the sand grade and the clay grade; the proportion of silt grade should be negligible, as it reduces permeability and increases the bulk-density gradient. The moulding characteristics are determined by the mechanical grading, shape, and mineralogical constitution of the particles composing the two grades.

(1) *Mechanical Grading.*

A coarse, well-graded sand has a higher permeability and lower strength, and packs more uniformly than a fine, well-graded sand having the same grain-shape. Other conditions being equal, a coarse sand imparts a rougher finish to the surface of a casting than does a fine sand.

In the dry sand, the size of the individual particles in the clay grade affects the rate of development of green strength.

(2) *Grain Shape.**

The shape of the sand grains affects the bulk-density distribution—and therefore the permeability and strength—in the mould or core. Of two sands having the same average grain-size and equally well graded, the more angular sand packs less uniformly than the more rounded sand. Furthermore, the surface friability of the mould or core increases with increase of angularity of the grains.

(3) *Mineralogical Constitution.*

The sand grade should be composed wholly of quartz, as the presence of silicate materials such as feldspar and muscovite increases the liability of the sand to burn on to the casting, without improving the other moulding characteristics. Muscovite occurs as flakes, which tend to impart a laminated structure to the sand when it is rammed around the pattern.

The mineralogical constitution of the clay grade determines the slopes of the permeability/moisture, the green-strength/moisture, and the dry-strength/moisture curves; it also determines the relationship of the bulk density before compression to the moisture content of the moulding sand.

* Based partly on work published in reference 4; included here for completeness.

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EXPERIMENTAL WORK ON THE PRODUCTION AND USE OF RADIOGRAPHED STEEL CASTINGS FOR SERVICE AT HIGH PRESSURES.

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(Figs. 6 to 13 = Plates III. and IV.)

SYNOPSIS.

The paper describes a practical experiment in the production of castings for use in handling fluids at 350-atm. pressure.

The castings selected for the experiment were of such size and form as to lend themselves to production and radiography by existing equipment.

The paper discusses the economic and technical advantages attending the use of castings for this class of duty, and emphasizes that the principal deterrent to their widespread use in this way is the uncertainty as to the soundness of a casting. The use of radiography to provide the necessary assurance on soundness is tested on a number of castings, and the results of the practical experiments are analysed. Castings which passed the stringent acceptance tests were installed on high-pressure lines and their performance is under observation. A trial period of two years in service is visualized before any definite conclusions can be drawn.

The experiments described in the paper utilized very extensive radiographic examination of all castings produced. Such extensive and costly examination was considered justifiable and necessary for the first experimental castings, but a reduction in the extent of radiographic examination is considered essential for commercial development. The author visualizes that such reduction may be obtained by careful standardization of moulding and casting methods for each size and type of casting. Such standardization may eventually permit of the acceptance of castings which have been radiographed only in key positions.

Further investigation along these lines is contemplated on completion of the trial period of two years' service.

INTRODUCTION.

A RECENT paper presented to The Iron and Steel Institute * gave an account of an investigation into the application of radiographic technique to the improvement in quality of steel castings. The objects of the author's experiments were to assess the practical value of radiography to the engineer, and to indicate the manner in which improvements in casting quality might develop as a result of radiographic study of founding and casting methods.

The present paper gives an account of a practical attempt to use the radiographic technique in the production of high-quality castings for a specific duty.

High-Pressure Fittings.

The sphere of engineering in which it was desired to study the possible application of radiographed castings was that concerned with the provision of equipment for handling fluids at high pressures. The particular operating pressures were 250 and 350 atm.

The plants operating at these pressures employ a wide variety of fittings, ranging from very large

reaction vessels to small-bore tubing; included in the range of fittings are pipe systems with bores varying from 2 to 6 in. in dia. Such pipe systems naturally require a considerable number of fittings in the form of bends, tees, and crosses, and it was in the supply of such special fittings that the possibilities of radiographed castings were considered. It is quite obvious that no general application of castings to such high-pressure systems could be considered at the present stage of development of the foundry art. At one end of the scale of sizes the larger pressure vessels would be beyond the practical scope of any foundry. Of the smaller fittings, many are of symmetrical form, lending themselves to mass-production processes involving hot deformation (e.g., tubing), while other fittings are of such size, form, and wall thickness, that satisfactory radiography would at present be an impossibility.

General consideration of this high-pressure equipment did, however, indicate a range of fittings of such size and form that their production as sound steel castings would offer an attractive possibility.

* R. JACKSON : *Journal of The Iron and Steel Institute*, 1945, No. I., p. 225 P.

The production of such hollow fittings as bends, tees, and crosses by the orthodox forging methods is attended by certain disadvantages. These disadvantages are discussed below under three headings: (a) Technical, (b) Economic, and (c) Design.

(a) *Technical.*

In the simpler forms of pressure vessels and fittings, the principal stress is hoop tension. In more complicated shapes, additional stresses may be imposed by the internal pressure, but in all cases, the safety of the vessel or fitting depends on the satisfactory *transverse* mechanical quality of the metal.

Generally, in the production of hollow vessels by forging, the bulk of the hot-working imposed is in one direction. In many cases, it is impossible to hot-work the metal in more than one direction. Such unidirectional working has a pronounced effect on the structure of the metal and, in certain cases, a serious effect on the transverse mechanical properties. It is obvious, of course, that unidirectional hot-work will have the effect of altering the general form of the grains from polygonal to plate- or pencil-shaped grains. This type of deformation of the grain is one factor in the deterioration of the transverse mechanical properties, particularly the ductility values. It is presumed that this reduction in ductility arises from the fact that the substantial change in form of the grains will obviously reduce the facility for deformation by reducing the number of gliding planes on which slip (*i.e.*, deformation) can occur. It seems certain that there are other factors contributing to the reduced transverse ductility, but no complete study has been made of them and it is not proposed to discuss the various theories in this paper.

From the foregoing it will be seen that the forging of internally stressed fittings introduces an important factor which does not concern normal externally stressed parts. In the case of the latter, hot-working in one direction to produce elongation in the direction of the principal service stress (*e.g.*, rolling bar to produce bolts or studs) enhances the mechanical properties. It is roughly true to say that a given improvement in the longitudinal properties by hot-working is paid for by a proportionate decrease in the corresponding transverse values within a wide ratio of original-ingot section to finished-bar section.

It should be appreciated that these remarks on transverse mechanical properties do not apply with equal force to all forms and sizes of hollow fittings. For example, the manufacture of a large hollow vessel does not result in deterioration of the transverse mechanical properties, although the hot-working is largely unidirectional. In this case, although the hot-work is all in the direction

of elongating the original billet, it is applied to both sides of the wall of the vessel—*i.e.*, the original billet is a hollow. Thus, the general shape of the grains is that of a plate rather than a pencil, and the operation does not result in serious deterioration of the transverse properties. In both the manner of working and the results, the operation is obviously closely allied to the rolling of a plate. While the longitudinal and transverse properties are not appreciably affected by this form of crystal deformation, the “depth” properties are seriously affected.

At the other end of the dimensional scale, small fittings can generally be produced by a forging technique which leaves the transverse mechanical properties unimpaired. This technique demands the application, at some part of the forging operation, of hot-work at right-angles to the general direction of working. With small forgings this imposition of transverse work can readily be achieved, but there is a definite size limitation on the billets which can be handled in this way. Further, certain common types of fitting—*e.g.*, tees and crosses—do not lend themselves to this technique.

The discussion above postulates the existence of massive metal in which the mechanical properties are similar in all directions. This is approximately true in the case of cast metals. The departure from the strict ideal arises principally from inhomogeneities in the metal; such inhomogeneities are not inherent in the metal itself but in the limitations imposed by the melting and casting technique. The distribution, location, and influence of such inhomogeneities can be controlled to a considerable extent by variations in the casting technique.

With the limitations outlined in the previous paragraph, it will be seen that certain advantages might be derived from the use of cast metals in the form of pressure vessels or fittings. If methods could be devised to eliminate or reduce the effect of the inhomogeneities normally present in cast metals, an approach could be made to the ideal pressure vessel. Clearly, any attempt to control the number and distribution of normal casting defects (pores, slag inclusions, drawn holes, &c.) must be guided by a full knowledge of their distribution for each variation in casting technique. One reliable method of obtaining such guidance is by the use of radiography. This investigation visualizes the extensive use of radiography to ascertain if suitable casting methods can be evolved for the regular and reliable production of sound steel castings.

(b) *Economic.*

The forging process has certain obvious limitations in shaping metals, and its use for high-pressure fittings demands a considerable amount

of machining as a final operation. This necessity is a particularly serious item in those fittings which are too small to permit of hollow forging. In such cases, the degradation to cheap scrap of a considerable proportion of the weight of the forging should be a matter of some concern.

From this point of view, castings offer obvious advantages. These advantages, however, have to be paid for by the cost of radiography. If experience had proved that complete radiography of each casting was necessary, the potential saving would be largely dissipated. It is the ultimate intention of the investigation to provide an answer to two questions:

(1) Can steel castings be produced to a degree of soundness permitting trial of such castings on high-pressure duty? The answer to this

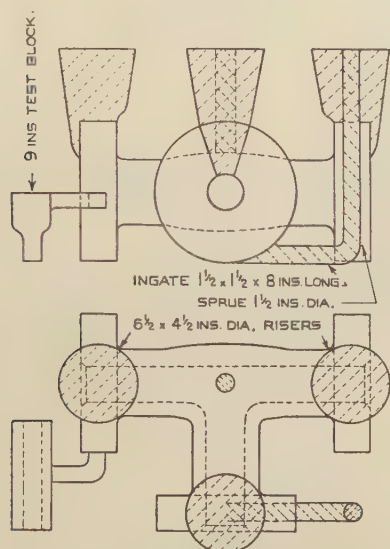


FIG. 1.—Casting and Feeding Arrangements for 3-in. Equal Tee.

question will be provided by extensive radiographing of all of a small number of trial castings.

(2) Can the experience gained under (1) justify the trial of castings which have only been radiographed in key positions? The location of the key positions will be dictated by experience under (1). Further, this experience will enable comparison of various techniques to be made, and selection of the technique best adapted for production of each general type of casting, *i.e.*, bends, tees, crosses, &c. It should be emphasized that no extensive use of castings over a wide variety of sizes and forms is visualized. It is intended to confine the investigation and any subsequent practical trials to those forms and sizes which offer a good combination of technical and economic

advantage. Examples of such fittings are bends, tees, crosses, &c., of 2–6 in. bore. For an indication of the size of such fittings, reference should be made to Figs. 1 and 2.

In connection with production, there is the question of speed of delivery. In any large constructional programme, or in an urgent constructional job, a saving in delivery time might be a considerable advantage. Experience has shown that in such cases, the manufacture of the smaller high-pressure fittings is frequently a limitation in this respect.

(c) Design.

To the economic advantages of production may be added certain considerations of design. With cast fittings, the right-angle elbow produced by

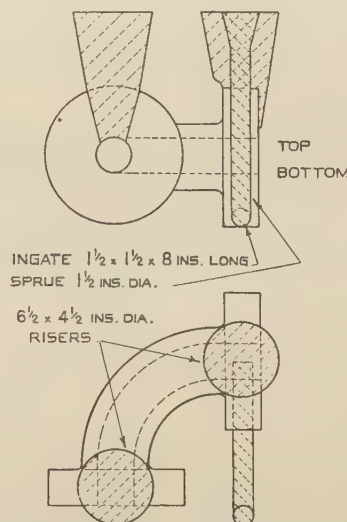


FIG. 2.—Casting and Feeding Arrangements for 3-in. Bend.

forging can be replaced by the cast bend, with consequent reduction in pressure drop. Further, the cast design can have the flanges cast integral with the body, thus eliminating the machining necessary for fitting high-pressure flanges.

FIRST ORDER FOR CASTINGS.

The first obvious necessity was to obtain the co-operation of a firm with the necessary foundry and radiographic equipment. Such co-operation was readily obtained and utilized throughout the investigation. The first order was for a small number of castings of varied form. They were to be produced from electrically melted steel containing 0.20–0.25% of carbon, and were to be fully radiographed. Details of the castings and the

number of radiographs required on each are given below :

Item.	Description.	Number of Radiographs.
A	3-in. equal tee	12
B	3-in. right-angle bend	12
C	2-in. equal tee	8
D	2-in. right-angle bend	8

Additionally, the finished castings had to be tested to a pressure of at least 6000 lb./sq. in. It was not considered advisable to specify rigid mechanical properties, but to examine and consider each case separately.

The order was placed in war-time and during a period when the foundry was heavily engaged in direct production of war supplies. Inevitably, this state of affairs led to delays in the production of a small special order, and also rendered difficult the provision of close and continuous technical supervision such as would normally be accorded to a development of this kind.

Moulding, Casting, and Testing Procedure.

Moulding and Casting Methods.

The moulding technique was quite normal for good-quality steel castings and the castings were all made by ordinary static methods. The casting and feeding arrangements for item *A* are shown in Fig. 1 and those for item *B* in Fig. 2. Items *C* and *D* were cast under similar conditions to those shown in Figs. 1 and 2, respectively.

Heat-Treatment.

All castings were annealed at 950° C. for 4 hr.

Mechanical Testing.

The test-block shown in Fig. 1 was used to provide test-pieces from which the mechanical-test results were obtained. These are recorded for all four items in Table I. Several attempts were made before completely satisfactory castings of items *C* and *D* were produced. Mechanical tests were taken on all the castings of these two items,

in both cases from the integrally cast test-pieces. These results, together with the reasons for rejection of the unsatisfactory castings, are also shown in Table I.

Analysis.

The composition of each casting was determined by analysing a sample from the appropriate cast of steel. On the strength of these results (shown below) all the castings were considered satisfactory and passed on for further examination. The analyses given for items *C* and *D* are those of the two accepted castings. However, the analyses of those castings which were rejected were quite normal and revealed nothing which could connect rejection with composition.

	Item A.	Item B.	Item C.	Item D.
Carbon, %	0.24	0.27	0.21	0.21
Silicon, %	0.23	0.34	0.25	0.34
Sulphur, %	0.046	0.033	0.018	0.031
Phosphorus, %	0.038	0.036	0.023	0.035
Manganese, %	0.79	0.67	0.57	0.62

Radiography.

The radiographic work was done throughout with a Phillips unit of two 150-kV. generators in Villard circuit.

Item A.—The arrangements for radiographing are shown in Fig. 3 from which it can be seen that the casting has been adequately "covered", and particular attention has been given to those locations which might be expected to show defects in an unsound casting, *e.g.*, the junctions of sections in different planes and the bases of feeding heads. Examination of the first batch of radiographs suggested that the definition could be improved, particularly in some of the key sections. A repetition of these radiographs (and all the subsequent radiographs) incorporated a penetrameter which showed a sensitivity of 1–2% of the wall thickness, which was considered reasonable. Only one small defect—in the region of one of the drilled bolt holes—was detected,

TABLE I.—*Details of Mechanical-Test Results.*

Item.	Yield Stress, tons/sq. in.	Ult. Stress, tons/sq. in.	Elong., % (on 4√A.).	Red. of Area, %.	Bend, degrees.	Reason for Rejection.
A . . .	20.4	34.2	28.0	46.4	130	...
B . . .	17.6	31.4	26.0	34.0	180	...
C (1) . .	16.4	29.6	27.0	38.8	130	Error in machining.
(2) . . .	19.6	31.6	26.0	40.0	180	Defects shown by radiographs.
(3) . . .	22.4	34.4	27.0	41.2	180	Defects shown by radiographs.
(4) . . .	24.0	38.0	19.0	19.6	46	Mechanical-test results.
(5) . . .	18.8	31.0	28.0	47.6	180	...
D (1) . .	18.4	30.0	30	33.6	180	Defects shown by radiographs.
(2) . . .	18.8	31.0	28.0	47.6	180	Defects shown by radiographs.
(3) . . .	22.8	33.6	28.0	43.6	120	Defects shown by radiographs.
(4) . . .	15.2	28.8	24.0	34.8	180	...

and this was cut out, welded, machined, and again radiographed. This batch of radiographs was then approved.

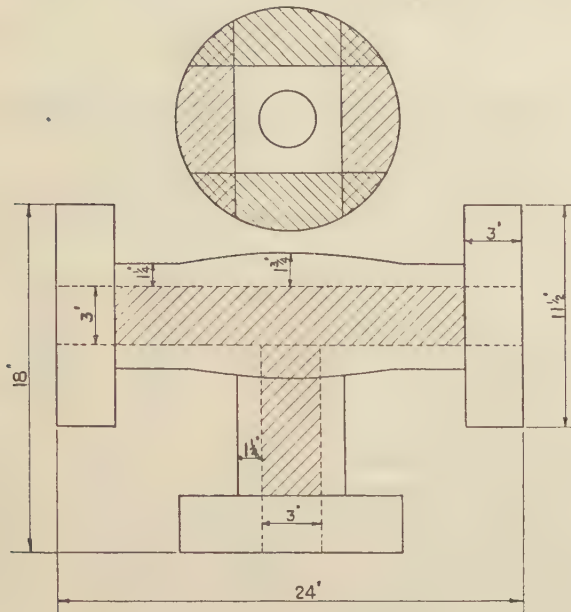


FIG. 3.—Typical Radiograph Locations for 3-in. Equal Tee.

Item B.—Fig. 4 shows the radiographing arrangements for item B. It will be seen that all the important parts of the casting have again been adequately covered.

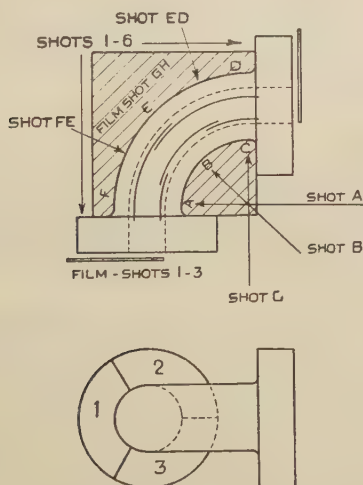


Fig. 4.—Typical Radiograph Locations for 3-in. Bend.

These radiographs revealed one small defect in a flange; this defect was cut out, and the preparation examined. On approval, the defective zone was welded up and again radiographed. A satisfactory radiograph was obtained.

Item C.—The accepted casting (No. 5, Table I.) of item C was radiographed in a manner similar

to that shown in Fig. 3. The normal examination was supplemented by "shots" taken with the film inside the drilled bolt holes.

The initial set of radiographs showed a good standard of soundness, but some doubt was felt as to markings on the film which might have been attributed to surface irregularities on the pipe portion of the casting. In order to clear up this point, it was decided to increase the bore of the casting by $\frac{1}{8}$ in., by machining in the doubtful region, and also to grind outside in the same locality. Care was taken to ensure that the sections of different dimensions were blended smoothly after machining. Another set of radiographs was taken and showed complete soundness except for one small inclusion in the wall of the casting. This was not considered sufficient for rejection.

Item D.—The radiographing procedure was similar to that of item B. As a result of the radiographs, three small welding repairs were made on the final casting. These repairs were checked radiographically, and the casting was accepted.

Pressure Testing.

After radiographing, the castings were subjected to pressure testing, using paraffin. Items A and B were tested at 6500 lb./sq. in., and items C and D at 7500 lb./sq. in. All the items were accepted on completion of this test and were subsequently installed into service at 350-atm. pressure. The performance of the castings during this high-pressure duty is at present under observation, the first casting having been installed in March 1944.

Summary of Results of the First Order for Castings.

Of the four castings ordered, two passed the very stringent tests required without difficulty. On both the smaller castings, several attempts were made before a satisfactory fitting was produced. It is hardly likely that the difference in size was responsible for the marked difference in results between the 3-in. and the 2-in. fittings. From the casting point of view, both are of the same order of size, and the smaller would not involve any special problems peculiar to themselves. It is important to note that several apparently sound castings were shown by radiography to be insufficiently sound for high-pressure duty.

These castings were produced by normal good foundry technique, were statically cast, and were not accorded any special degree of technical supervision. They were, of course, fully radiographed, but this examination was in the nature of an acceptance test only, since no modification of moulding or casting technique was made as a result of radiography.

In the light of the special war-time difficulties associated with any development work, and certainly associated with this casting investigation, the results achieved were considered worthy of further work.

SECOND ORDER FOR CASTINGS.

In considering the course to be followed subsequent to the completion of the first order, two factors of importance were borne in mind :

(1) The advantages of centrifugal casting had already been discussed with the founders associated with this investigation, who had installed suitable machines for this method of production.

(2) The first order covered a variety of shapes and sizes. A closer study of one particular size and form of casting would enable a better judgement to be formed of the possibility of repeating regularly, with an established technique, the degree of soundness demanded. Such a study is, of course, necessary in order to reduce to reasonable limits the amount of radiographing demanded for each casting. Obviously, if a given technique could be proved to yield regularity of soundness over a considerable number of castings, consideration would be given to cutting down the number of radiographs to cover only the more doubtful locations.

In these circumstances it was decided to place an order for eight 2-in. bends similar in all respects to item *D* of the first order. All details of composition, heat-treatment, and radiographing were to be identical with those of the first order. The only significant difference, therefore, was that the castings of the second order were produced by centrifugal-casting methods. From the batch of castings so produced it was proposed to select one or two representative ones, after the whole batch had been fully tested and accepted, to be cut up for detailed metallurgical examination.

The castings for the second order were produced from metal melted in a high-frequency induction furnace.

All castings were fully radiographed along the lines adopted in the original order. The radiographs were used, not only for orthodox assessment of soundness but also in the selection of two castings required for detailed examination. The radiographs of these two castings were further used as a guide in taking metallographic samples.

It will be appreciated that some correlation of the results of radiographic with metallographic examination was necessary, since it could not be assumed, with safety, that the comprehensive experience and detailed knowledge acquired on Class I. welding was entirely applicable to castings.

Fundamentally, interpretation of radiographs should be the same in castings as in welding, but certain detailed defects peculiar to castings would require special study.

Testing Procedure.

The castings progressed through the foundry and were tested in the normal manner.

Analysis.

The analyses of samples taken from the casts were as follows :

	Cast 1502. (3 castings)	Cast 2054. (3 castings)	Cast 2176. (3 castings)
Carbon, % . . .	0.19	0.25	0.27
Silicon, % . . .	0.24	0.34	0.34
Sulphur, % . . .	0.014	0.020	0.015
Phosphorus, % . .	0.015	0.018	0.015
Manganese, % . .	0.53	0.64	0.69

Mechanical Testing.

Tensile and bend test-pieces were machined from separately cast test-bars, each of the three casts of which the analyses are given above providing material for one set of tests. The results were considered satisfactory :

	Cast 1502.	Cast 2054.	Cast 2176.
Yield stress, tons/sq. in. .	20.0	22.4	21.6
Max. stress, tons/sq. in. .	30.8	37.0	36.4
Elongation, % (on $4\sqrt{A}$). .	21.0	22.0	24.0
Reduction of area, % . . .	30.0	32.4	36.4
Bend, degrees	120	120	120

Pressure Testing.

After mechanical testing, all castings were subjected to internal pressure testing at 7500 lb./sq. in. All eight castings withstood this test satisfactorily.

Radiography.

Examination of the pipe portion of each casting was made by inserting the film into the bore and shooting the rays through a single wall of the casting. Each pipe was covered by eight separate radiographs.

The flanges of each casting were examined after machining and drilling the bolt holes. Each flange was completely covered in two shots. There were thus twelve radiographs per casting. In order to "block" the outline of the flanges during shooting, the flanges were immersed in a concentrated solution of lead salts. This method carries with it the danger of trapping air bubbles against the casting, with possibilities of confusion in interpretation. In fact, trapped air bubbles were detected in certain cases, and their presence was established by taking repeat shots.

Details of the penetrameters used and the sensitivity obtained are as follows :

Penetrameters for Flanges.—Ten wires decreasing in diameter by equal steps from 0.100 to 0.010 in.

Penetrameters for Pipe.—Ten wires decreasing in diameter by equal steps from 0.050 to 0.005 in.

Section.	Wire Visible, in.	Sectional Thickness, in.	Sensitivity, %.
Pipe . . .	(8th) 0.015	0.75	2
Flange . . .	(8th) 0.030	2.0	1.5

Four of the castings showed particular freedom from defect. Two others had defects of a minor nature. The remaining two castings showed more defects, or possible defects, and it was decided to subject these two to detailed metallurgical examination, in accordance with the pre-arranged plan.

DETAILED EXAMINATION OF TWO SELECTED CASTINGS.

Radiographs.

Casting 2054/2A.—The set of radiographs covering this casting showed two defects, one on the flange and one on the pipe portion. Both defects were small and of such a nature that reproduction from the negatives would not provide satisfactory illustration of the defects.

Casting 2176/2B.—The flanges of this casting showed one defect. Two defects appeared on the pipe portion and these are reproduced in Fig. 6.

It should be remembered, in examining these photographs, that prints of radiographic negatives are not generally regarded as satisfactory for the study of defects; such study is always done on the original negatives. The sharp black line on the prints represents a surface projection.

Sectioning of Castings.

On the basis of the radiographs, the castings were sectioned as shown in Fig. 5. The double lines indicate the planes from which micro-sections were taken. Opportunity was taken to provide mechanical-test test-pieces as shown.

The general soundness of the castings is illustrated by the macro-etched section shown in Fig. 8.

Mechanical Testing.

Test-pieces cut as shown in Fig. 5 gave the following results:

	2176/2B.		2054/2A.	
	Longi-tudinal.	Trans-verse.	Longi-tudinal.	Trans-verse.
Yield stress, tons/sq. in.	24.0	27.0	25.0	28.0
Max. stress, tons/sq. in.	37.0	38.0	38.0	37.5
Percentage elongation on $4\sqrt{A}$	24.0	20.0	23.0	23.0
Reduction of area, %	40.0	31.0	36.0	41.0
Izod, ft. lb.	32, 20	34	28, 26	26
Vickers hardness number	185	184	184	182

These results are considered very satisfactory and reveal the homogeneity of the material and the absence of any appreciable difference between longitudinal and transverse properties.

Micro-Examination.

Fig. 7 illustrates the well-refined, normal structure of the castings.

Casting 2054/2A.—Micro-examination was made on this casting on all the planes shown in double

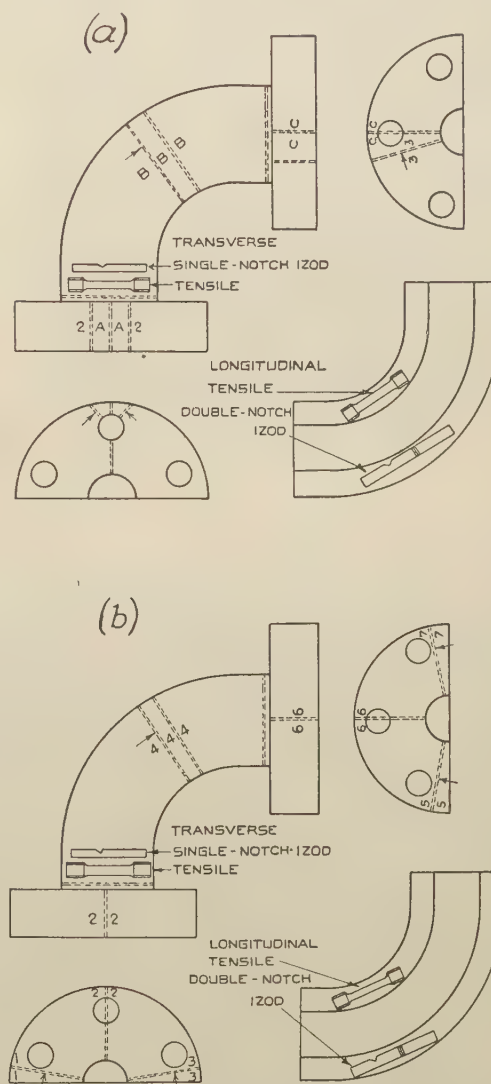


FIG. 5.—Two Selected Castings, showing sections chosen for micro-examination and areas from which test-pieces were taken, (a) 2054/2A and (b) 2176/2B.

lines in Fig. 5. In no case did the examination reveal any significant defect. The casting can, therefore, be judged sound, even by the exacting standards to which it was examined.

Casting 2176/2B.—The detailed examination of

this casting revealed several defects. Three cuts were made in the flange, one of them coinciding, as nearly as possible, with the apparent defects shown on the radiographs. No significant defects were found but some scattered fine porosity was shown on the plane of section 1 (Fig. 5). This section is shown as a macrograph in Fig. 9. A typical porous zone, consistent with the radiograph, is shown in Fig. 10.

The tubular portion of the casting was cut in two places at section 4 (Fig. 5). Fig. 12 is a macrograph of the worst area of subcutaneous porosity revealed. Examination of the area of porosity at higher magnification showed that the pores were mostly of the spherical, gas-generated type, as illustrated in Fig. 11.

Summary of the Results of Micro-Examination.

One of the castings selected for examination proved to be substantially sound and to have no significant feature worthy of record.

The second casting showed defects of two types :

- (1) Interdendritic porosity located on the edge of the flange.
- (2) Scattered porosity, in the form of spherical gas holes in one region of the tubular portion.

Neither type of defect would have been considered cause for rejection, in the degree and distribution revealed.

Dimensional Accuracy.

In cutting up the two castings, attention was given to the dimensions of the various sections. Generally the thickness dimensions on the cut planes was satisfactory, but one exception was noted on casting 2176/2B. In the tubular portion, an area of reduced thickness was observed (Fig. 13). On the outside wall a smooth depression about 2 sq. in. in area was noted. The reduction in thickness at the bottom of the depression amounted to 5.5% of the nominal wall thickness. The change in thickness was smooth and gradual, and was not accompanied by any defects. Nevertheless, it is an additional feature of criticism which, taken along with the other defective features in this casting, indicates that a considerable measure of care is still required in the allocation of these special steel castings for high-pressure duty.

FINAL CONCLUSIONS.

Of the total of eight castings delivered in the second order, seven have been shown as acceptable to a standard which is high, but which is considered necessary for the severe duty to which the castings will be subjected. The eighth casting was not of such a high standard. Further development of this work may justify a reduction in the amount of radiography, but it is not intended to reduce the radiographic standard of acceptance.

It has been seen that with two of the castings of the original order it was necessary to make several attempts before satisfactory results were achieved. In view of the high standard set, this was not surprising. It will be noted that more consistent results were achieved with the second order of eight similar castings which were produced by the centrifugal-casting process.

Several of the castings have been on 350-atm. service (cold) for periods up to 22 months, and, up to date, have performed satisfactorily. It is proposed, however, not to attempt to draw definite conclusions until the whole batch of castings has been in service for a period not less than two years. In the event of the service performance giving justification for continuing the development, it is planned to proceed along lines which may justify reduction in the number of radiographs per casting. For this purpose each size of each type of casting (*i.e.*, tee, bend, or cross) will be regarded as a separate founding problem, and pattern, moulding, and casting technique, and radiographic procedure will be developed for each particular case. Naturally, the development will be a gradual one, spread over several years, but it is hoped that eventually a dependable supply of high-quality castings will be assured.

As a corollary to this development, the gradual introduction of radiography into the foundry is expected to produce an all-round improvement in the quality of the general supply of engineering castings.

ACKNOWLEDGMENT.

The author wishes to acknowledge, with gratitude, the wholehearted co-operation of Messrs. David Brown & Sons (Huddersfield), Ltd., and the help and encouragement of Mr. J. F. B. Jackson, Technical Controller of Messrs. David Brown's foundries at Salford and Penistone. Without this co-operation and assistance the work could not have been done.

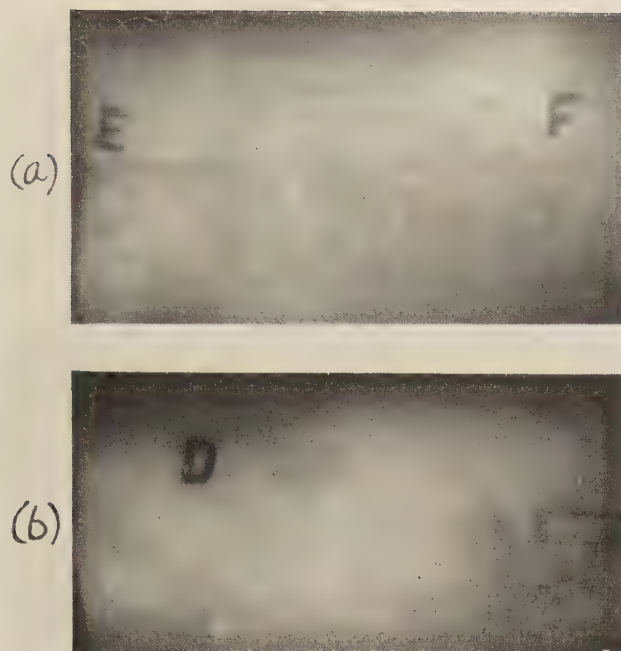


FIG. 6.—Radiographs of Defects in the Pipe Portion of Casting 2176/2B.



FIG. 7.—Microstructure of the Selected Castings.



FIG. 8.—Macro-Etched Section of the Selected Castings, showing the general soundness. (Approx. $\times \frac{1}{2}$.) (Reduced to seven-eighths linear in reproduction.)

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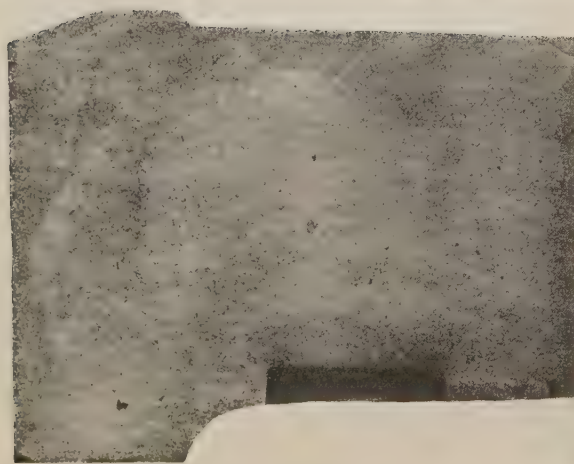


FIG. 9.—Macrostructure of Flange Section, showing scattered porosity. (Approx. full size.)



FIG. 10.—Unetched Microsection of a Typical Porous Zone of Casting 2176/2B. $\times 20$.

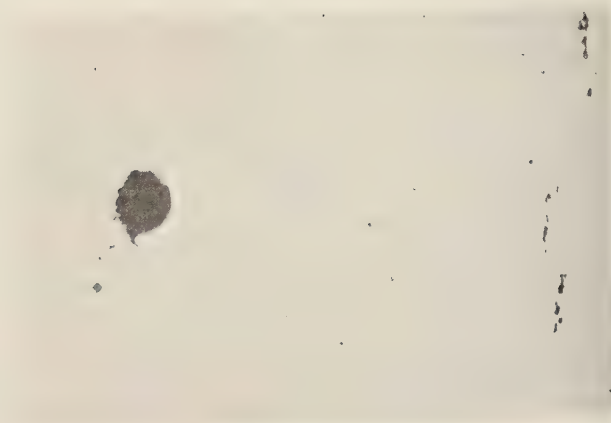


FIG. 11.—Casting 2176/2B; subcutaneous porosity of the spherical, gas-generated type. $\times 10$.



FIG. 12.—Macrograph of the Worst Area of the Pipe Section of Casting 2176/2B, showing subcutaneous porosity. (Approx. full size.)



FIG. 13.—Macrostructure of Pipe Section of Casting 2176/2B, showing local reduction of wall thickness.

THE RAPID DETERMINATION OF REACTIVE OXYGEN IN OPEN-HEARTH STEEL.*

By I. M. MACKENZIE, B.Sc. (MESSRS. COLVILLES, LTD.).

Paper No. 36/1946 of the Ingot Committee (submitted by the Chemists' Panel of the Sub-Committee on Gaseous and Non-Metallic Inclusions).

SYNOPSIS.

An experimental method of determining the reactive oxygen in liquid steel is described. The results so obtained are shown to correlate with the carbon content and the rate of carbon drop. A formula expressing the relationship is derived enabling the reactive oxygen, during the later stages of the boil, to be calculated or determined graphically from the carbon-drop curve.

INTRODUCTION.

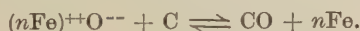
SEVERAL methods of determining the oxygen content of liquid steel are available.¹ Most of them suffer from a dual disadvantage. Firstly, the value given is that of total oxygen, including that present in inclusions and, secondly, the determination takes too long to be of assistance in melting-shop practice.

A quick method of determining the degree of oxidation of the metal towards the end of the boil would find an application in the control of the subsequent deoxidation. Work has therefore been carried out on the method proposed by Schenck,² in which the concentration of oxygen in the iron phase is calculated from the concentration of carbon and the rate of carbon drop.

METHODS OF OXYGEN DETERMINATION.

Theory of the Calculation of Oxygen in Steel.

During the refining process, carbon is removed by a reaction of the type :



If the velocity constants for this reaction are k_1 and k_2 then :

$$\frac{d[\text{C}]}{dt} = [\text{O}] [\text{C}] k_1 - k_2 p_{\text{CO}} \quad . \quad . \quad (1)$$

which may be written :

$$[\text{O}] = \frac{\frac{d[\text{C}]}{dt} + k_2 p_{\text{CO}}}{[\text{C}] k_1} \quad . \quad . \quad (2)$$

where $[\text{C}]$ and $[\text{O}]$ are percentage concentrations of carbon and oxygen.

The above formula is not based on any hypo-

thesis of the mechanism of the carbon/oxygen reaction. Its validity can only be shown by demonstrating that it correctly represents the relationship between observed values of the three variables.

The work of Marshall and Chipman³ has shown that the activities of carbon and oxygen vary with increasing carbon concentration. However, to assist control in steelmaking, determination of the oxygen content of the bath is required only for carbon contents between 0.07 and 0.7%, and in this range the product $[\text{C}] \times [\text{O}]$ has been found to be nearly constant.

The rate of carbon drop, $d[\text{C}]/dt$ (per cent/min.), can be determined from the gradient of the curve obtained when carbon content is plotted against time, and p_{CO} is the partial pressure of carbon monoxide in contact with the steel. The bubbles in the steel will be at a pressure a little above atmospheric and consist of an equilibrium mixture of CO and CO_2 . As only about 2% of the gas formed will be CO_2 this may be neglected³ and, as the value $k_2 p_{\text{CO}}$ is determined directly by experiment, a knowledge of the actual pressure of CO in contact with the steel is not required. The reaction velocity constants k_1 and k_2 must be determined by experiment.

Work on the carbon/oxygen equilibrium in molten iron, carried out by Phragmen and Kalling,⁴ showed that the constants vary only slightly, if at all, in the range of temperatures encountered in open-hearth practice ($1600^\circ \text{C.} \pm 40^\circ$). This is confirmed by the theoretical calculation of the variation from the heat of reaction.

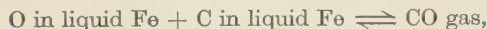
Since

$$\log_e K = -\frac{\Delta H}{RT} + \text{entropy factor},$$

* Received March 29, 1946. This paper is published by authority of the Ingot Committee. The views expressed in it are the author's, and are not necessarily endorsed by the Committee as a body.

we can calculate the fractional change in K for a 10°C. change in temperature about the mean temperature of 1600°C.

For the reaction :



ΔH has a value of about 5000 cal./mol. This gives a variation of about 0.6% per 10°C. which is well within the limit of experimental error, even for a range of 80°C. about the mean temperature. In high-temperature reactions the kinetic energy of the molecules is always well above the critical value for reaction, so that any small alteration in temperature makes little difference to the reaction rate.

Schenck² has given a table of values of k_1 and k_2 which he found to be independent of temperature but to vary with carbon content. The present author found that these values did not give satisfactory results above 0.3% of carbon, and therefore the constants have been redetermined.

Experimental Method.

The oxygen content was determined at various times during the boil in acid and basic furnaces of 60 and 100 tons' capacity. As these furnaces were producing plain carbon or low-alloy steels, the residual content of alloying elements was low. As the addition of ore or lime might be expected to produce temporary heterogeneity of the bath, samples were not drawn within 10 min. of any addition.

The method employed for obtaining samples was the "closed bomb" method as described by Swinden.¹ The bomb contained 5 g. of 30-gauge aluminium wire, and was closed by a thin mild-steel cap. After slagging up to the neck for 5 sec. the bomb was held beneath the surface of the metal for 10 sec. When cold, the bomb was opened and drillings were taken from the bottom half of the solid sample.

The alumina content was determined by the nephelometric method.¹ This method was chosen because it was considered to give the best determination of the oxygen in the iron phase, *i.e.*, reactive oxygen. It is improbable that inclusions in the steel would be reduced by aluminium in the short time for which the sample is molten.⁵ In the nephelometric determination, the absorption of light will depend primarily on the number of particles of alumina formed from oxygen in the metal. The instrument used was a Spekker photo-electric absorptiometer, using Ilford filters No. 607 and an instrument setting of water-to-water 1.0. The presence of chromium interferes with the results and a correction must always be applied to allow for the effect of this element.

The calibration curve for the nephelometric analysis was obtained by plotting absorptiometer drum readings for a number of selected bomb

samples against the percentage of alumina as determined by the 8-hydroxyquinoline method :

Ten grammes of drillings are dissolved in a mixture of orthophosphoric and nitric acids, the solution is then boiled with ammonium persulphate and is filtered when cold, through tightly packed pulp. The impure residue is ignited, and is then fused with potassium bisulphate. The fused mixture is extracted with water, and iron removed by precipitation with excess boiling sodium hydroxide. The solution is made acid, and a slight excess of 8-hydroxyquinoline in 2N acetic acid is added. Precipitation is completed with 2N ammonium acetate. After standing for 1 hr. the precipitate is collected on a sintered glass filter and is washed well with cold water. The precipitate of $\text{Al}(\text{C}_9\text{H}_6\text{ON})$ is dried at 120°C. and weighed. The factor for conversion to Al_2O_3 is 11.10%.

Certain bomb samples which were analysed by the gravimetric method gave anomalous results, while the nephelometric and calculated values were in good agreement. This could not be explained, but it suggests that the gravimetric method is less reliable than the nephelometric method for the determination of reactive oxygen.

Carbon/time curves were plotted for each charge, using data from the melting-shop log-book. The accuracy of this data was confirmed by taking a number of extra samples for carbon analysis. For each sample, the rate of carbon drop was determined from the gradient of the curve at the time at which the bomb sample was drawn.

Various values of k_1 and $k_2 p_{\text{CO}}$ were tried in equation (2), until the pair giving the most satisfactory calculated values for the oxygen concentration were found. The best values of the constants were found to be :

$$\begin{aligned} k_1 &= 1.90 \\ k_2 p_{\text{CO}} &= 0.005 \end{aligned}$$

These constants approximate to the values given by Schenck for low carbon concentrations, but the author finds that they give results correct to $\pm 0.002\%$ of oxygen up to 0.7% of carbon. At higher carbon contents the variation in the activity of the reactants becomes appreciable, and calculated values tend to be considerably low. The results are shown in Table I, and the calculated oxygen values are plotted against the drum readings of the absorptiometer, in Fig. 1. The points lie fairly closely on the straight line which is the calibration curve for the nephelometric analysis.

The agreement between calculated oxygen contents and those obtained by experiment for widely differing conditions of carbon content, rate of carbon drop, and temperature, indicates that the basic assumptions made by the author are correct; *i.e.*, the nephelometric analysis does determine reactive oxygen, and the constants k_1 and $k_2 p_{\text{CO}}$ are independent of temperature in the range found in steelmaking practice.

The oxygen contents of some of the bombs were

TABLE I.—Comparison of Oxygen Determination Methods.

Cast No.	Carbon, %.	Rate of Carbon Drop, %/min.	Oxygen, %.			
			Calculated.	Nephelometric Method.	Vacuum-Fusion Method.	Gravimetric Method.
C 956	0.07	0.0008	0.040	0.040	0.040	...
G9535	0.15	0.0014	0.023	0.022	0.030	...
F 493	0.15	0.0015	0.023	0.023	0.020	...
V8249	0.16	0.0043	0.031	0.031	0.027	...
Q6665	0.17	0.0017	0.021	0.021	0.016	...
Q6698	0.18	0.0015	0.020	0.021	0.018	...
F 297	0.27	0.0042	0.018	0.017	0.015	...
S3764	0.18	0.0044	0.027	0.025	0.032	...
U 645	0.14	0.0026	0.029	0.028	0.037	...
A9230	0.24	0.0026	0.017	0.016
E 696	0.12	0.0014	0.028	0.026	...	0.029
E 699	0.09	0.0021	0.042	0.039	...	0.051
G9341	0.15	0.0025	0.026	0.026	...	0.026
B9982	0.17	0.0010	0.019	0.019	...	0.023
U 713	0.18	0.0032	0.024	0.023	...	0.028
U 730	0.28	0.0046	0.018	0.018	...	0.020
F 369	0.30	0.0034	0.015	0.016	...	0.018
G9759	0.11	0.0013	0.030	0.029	...	0.034
V8115	0.51	0.0046	0.010	0.012	...	0.030
T 120	0.7	0.0042	0.007	0.008	...	0.020
X9378	0.30	0.0039	0.016	0.019
X9635A	0.57	0.0090	0.013	0.012
„ B	0.43	0.0050	0.013	0.013
„ C	0.30	0.0043	0.016	0.015
E1057A	0.425	0.0050	0.012	0.010
„ B	0.335	0.0045	0.015	0.013
„ C	0.27	0.0040	0.017	0.012
„ D	0.21	0.0032	0.017	0.017
„ E	0.17	0.0020	0.023	0.022
„ F	0.135	0.0012	0.024	0.023
A9308	0.64	0.0044	0.008	0.008
T 335	0.765	0.0060	0.008	0.008
E1060A	0.11	0.0010	0.027	0.027
„ B	0.08	0.0002	0.033	0.032
X9683A	0.74	0.0070	0.010	0.012
„ B	0.61	0.0050	0.009	0.010
W1052	0.425	0.0030	0.010	0.013
U1094	0.62	0.0060	0.009	0.009
Y1425A	0.43	0.0030	0.010	0.011
„ B	0.505	0.0020	0.007	0.010

also determined by vacuum fusion and by the gravimetric method described by Swinden.¹ These results are plotted against the drum

readings, in Fig. 2. The vacuum-fusion results (one set of determinations were made at the United Steel Companies, Ltd., and the other set

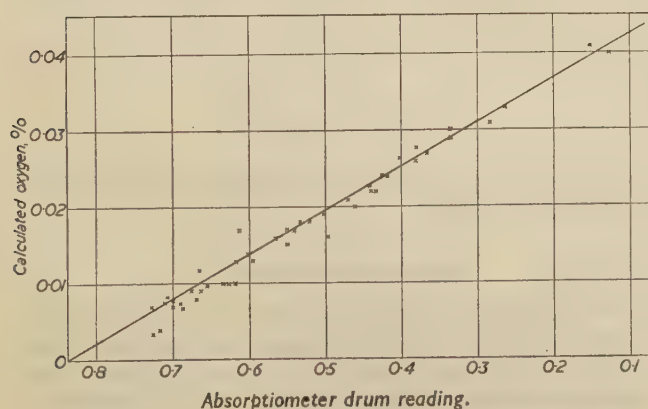


FIG. 1.—Calculated Oxygen Values Plotted on Nephelometric Calibration Curve.

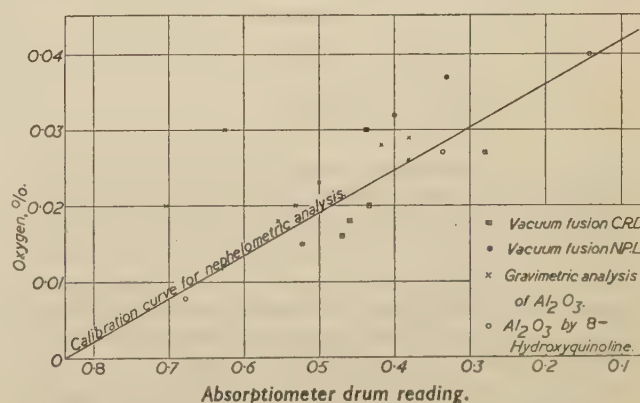


FIG. 2.—Comparison of the Results of Total Oxygen Determinations.

at the National Physical Laboratory) tend to be low, possibly owing to the presence of aluminium.⁶ The gravimetric results tend to be high. In general these results show greater scatter, probably owing to the presence of inclusions.

Graphical Determination of Oxygen from Carbon/Time Curves.

For the rapid oxygen determination without arithmetical calculation, the method proposed by Schenck² has been found satisfactory when the curves are plotted using the constants given by the author.

Ideal carbon/time curves are drawn for various fixed oxygen contents using the integrated form of equation (1):

$$t = \frac{1}{[O]k_1} \log_e ([O]k_1 [C] - k_2 p_{CO}) + c_1 \quad (3)$$

where the constant of integration, c , only determines the position of the curve on the time axis and can be ignored for the present purpose.

Substituting values for k_1 and $k_2 p_{CO}$ we have:

$$t = \frac{2.30}{1.9[O]} \log_{10} (1.9[O][C] - 0.005) \quad (4)$$

Taking successive fixed values of oxygen concentration, curves of carbon against time may be plotted, as shown in Fig. 3. The curves are

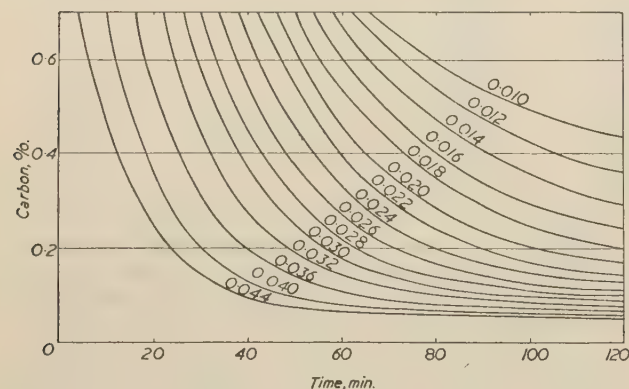


FIG. 3.—Carbon/Time Curves for Successive Values of Oxygen.

spaced along the time axis at convenient intervals. These curves are plotted on transparent graph paper, which is then superimposed on the actual carbon/time curve (*i.e.*, the melting-shop curve) plotted to the same scale. The transparent paper is moved along the time axis of the melting-shop curve until two gradients coincide for any chosen carbon content. Since there is a unique oxygen content for any particular condition of carbon content and rate of carbon drop, the oxygen content of the steel bath is given by the

oxygen percentage of the ideal curve with the same gradient at the carbon content considered.

THE CARBON/OXYGEN EQUILIBRIUM.

Putting $d[C]/dt = \text{zero}$ in equation (2) gives a constant product for the equilibrium concentrations of carbon and oxygen. The value $[C] \times [O] = 0.005/1.9 = 0.0026$, is in good agreement with the values determined by Vacher⁷ ($[C] \times [O] = 0.0025$ at 1580°C.) and Leiber⁸ ($[C] \times [O] = 0.0026$ at 1620°C.) who used a different

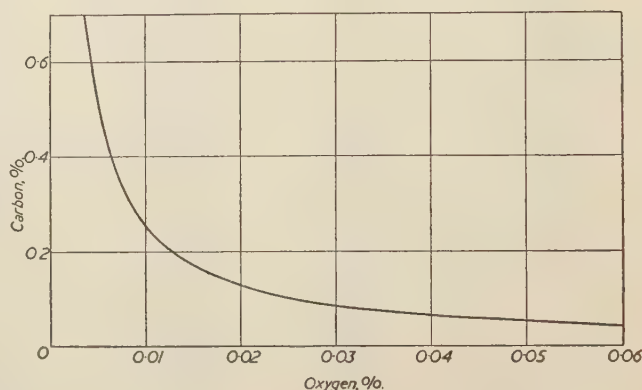


FIG. 4.—Carbon/Oxygen Equilibrium Curve ($[C] \times [O] = 0.0026$).

experimental method. Fig. 4 shows the equilibrium curve $[C] \times [O] = 0.0026$.

CONCLUSION.

Determination of the alumina in bomb samples by nephelometric analysis gives a measure of the reactive oxygen in liquid steel. Vacuum fusion and ordinary gravimetric analysis are affected by slag or inclusion contamination. The reactive oxygen content at any time during the boil may be calculated from the carbon content and the rate of carbon drop using the expression:

$$O, \% = \frac{\frac{d[C]}{dt} + 0.005}{1.9[C]}$$

or it may be determined graphically from the carbon/time curve.

ACKNOWLEDGMENT.

The author thanks the Directors of Messrs. Colvilles, Ltd., for permission to publish this paper. He also thanks his colleagues for their assistance, and particularly Mr. W. F. Charteris, Chief Chemist, Dalzell Works, for the chemical analyses.

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IMPROVEMENT IN DESIGN OF IMMERSION PYROMETERS FOR LIQUID-STEEL TEMPERATURES.*

BY D. MANTERFIELD, F.I.M., AND J. R. THURSTON (MESSRS. STEEL, PEECH AND TOZER, SHEFFIELD).

Paper No. 35/1946 of the Ingot Committee (submitted by the Liquid Steel Temperature Sub-Committee).

SYNOPSIS.

An improved design of immersion thermocouple, consisting of a semi-permanent fixture attached to the back-wall furnace binding and manipulated through the back wall of the furnace by means of a light jib, is described. The apparatus is easy to manipulate, requires only one operative, and its maintenance is of a very small order. Details of the construction and use of the apparatus are given, together with an account of its behaviour in practice.

A steel end block, which has an extremely long life and the use of which has eliminated troubles with embrittlement of the rare-metal couple wires, is also described. References are made to other improvements which are contemplated, including an all-steel arm for the back-wall installation.

INTRODUCTION.

THE quick-immersion thermocouple method of measuring liquid-steel temperatures has reached a stage in its development where it can confidently be used as a means of control in steelmaking practice. However, there is some diversity in thermocouple design at different plants and it is realized that improvements are possible in many directions. Among the minor disadvantages of thermocouple utilization are :

(1) The difficulties of conveying the apparatus from furnace to furnace on a large plant, over routes often obstructed by charging machines, rails, heaps of raw materials, &c.

(2) The considerable amount of maintenance required when the arm of the apparatus is protected by diatomite bricks or refractory paste.

(3) The physical discomfort of the operatives in taking temperature measurements while in proximity to a partially opened door.

(4) The embrittlement of the rare-metal couple wires.

THE BACK-WALL THERMOCOUPLE.

It has been realized that a permanent or semi-permanent thermocouple installation at each furnace would be a considerable improvement on the present types of equipment. One of the authors (J. R. T.) has devised and constructed an apparatus which is attached to the back-wall binding of the furnace and which overcomes many

of the difficulties and discomforts previously mentioned. The apparatus is easy to manipulate, requires only one operative, and its maintenance is of a very small order. With little modification the equipment could be applied to almost any type of open-hearth furnace and to many electric types; it could also be conveniently attached to an indicator or recorder. The constructional details lend themselves to some standardization, which circumstance should ensure availability of supplies and decreased initial cost.

Recent investigations^{1, 2, 3} into the distribution of temperature in various types of steel furnaces have shown the temperature variation to be small when the bath is active and that the variation in the horizontal plane is less than that in the vertical. In view of these facts the necessity of reaching to the middle of the bath in taking temperature measurements is not vital. A position midway between the back bank and the centre of the furnace, at a depth of 9 in. into the steel, would give a reading representative of the bath as a whole. A series of duplicate temperature measurements taken with the new apparatus and the trolley type showed a maximum discrepancy of 3° C. at these two points; in view of this the thermocouple arm can be made shorter and lighter, so making the apparatus easier to manipulate and maintain. If slag temperatures are required the depth of immersion could be manually adjusted, and for steel temperatures at a greater depth than 9 in. a correspondingly longer arm could be used.

* Received February 4, 1946. This paper is published by authority of the Ingot Committee. The views expressed in it are the authors', and are not necessarily endorsed by the Committee as a body.

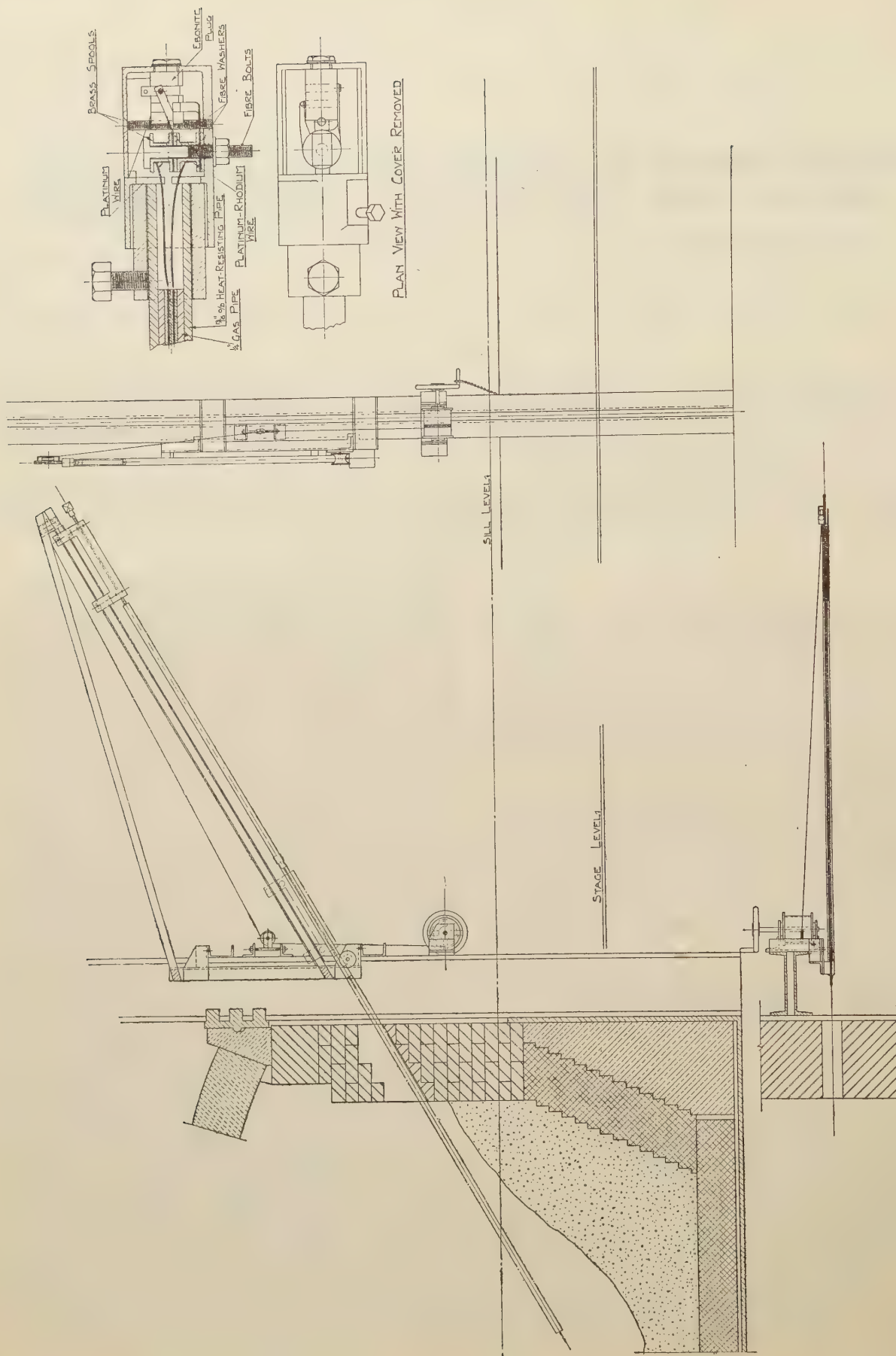
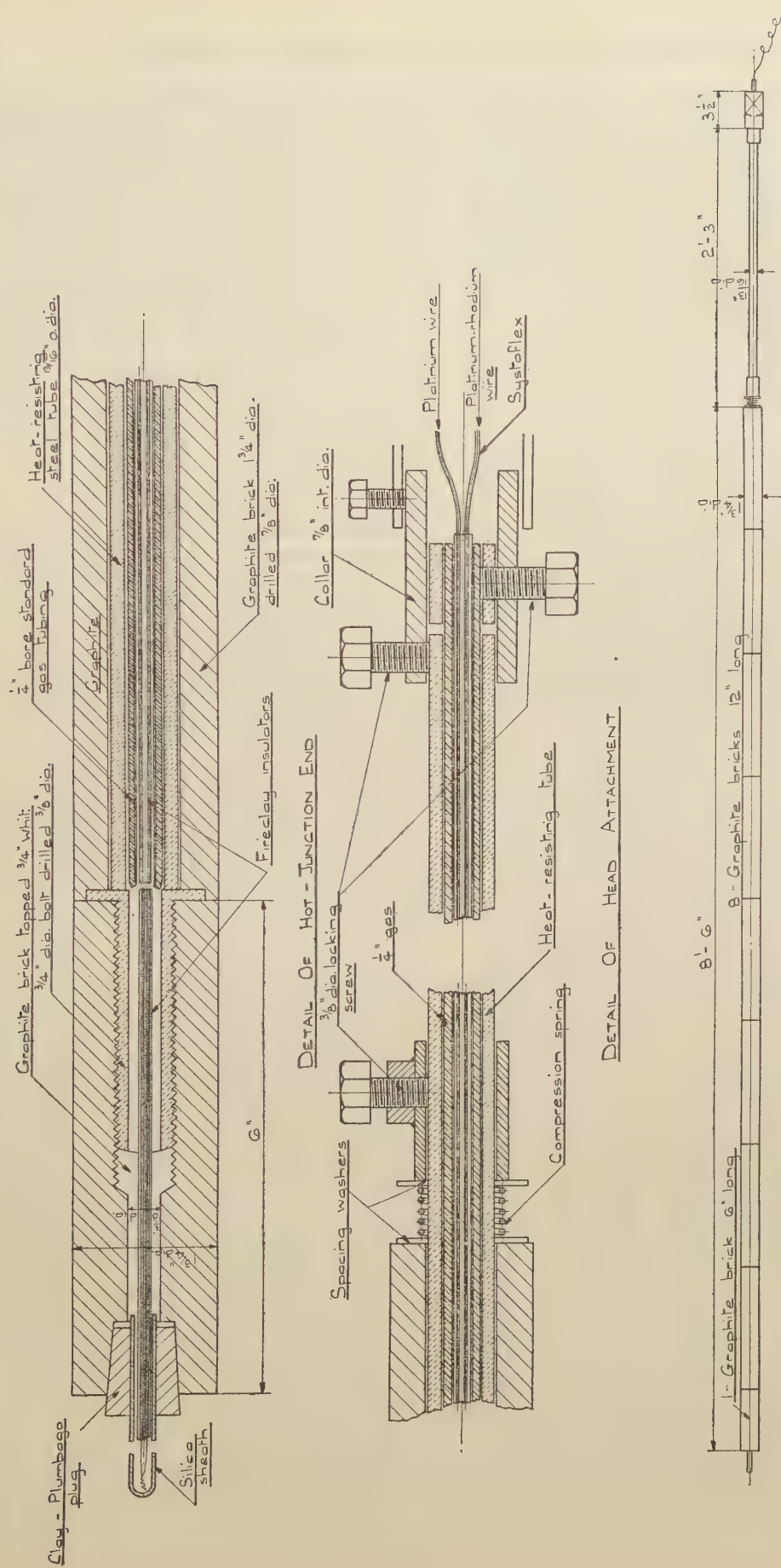


FIG. 1.—General Arrangement of Back-Wall Immersion Pyrometer.



ARRANGEMENT OF PYROMETER.

FIG. 2.—Arrangement of Pyrometer Arm and Details of Head Attachment.

An experimental instrument constructed of materials readily available on the works has been in use for some time. Various minor improvements on this apparatus were made and a more permanent and more precise instrument was finally designed and constructed. This latter instrument has now been in use for several months and has given complete satisfaction; details of the apparatus are given in Figs. 1 and 2.

The thermocouple arm consists of a heat-resisting steel tube, 10 ft. 1 in. long and $\frac{13}{16}$ in. in outside dia., protected from steel, slag, and flame along 8 ft. 6 in. of its length by means of plumbago sleeves, each 12 in. long and $1\frac{3}{4}$ in. in outside dia. The bottom sleeve is of graphite, 6 in. long, and is threaded for screwing to a $\frac{3}{4}$ -in. Whitworth set-screw, 4 in. in length, drilled longitudinally and stub-welded to the end of the main tube. The sleeves are kept rigid by means of a loaded spring, which allows for expansion; a collar is left on the set-screw to take the thrust of the spring. To prevent the percolation of liquid steel through the joints, these are sealed with plumbago paste, and the last sleeve is recessed. The rare-metal couple wires are run through twin-bore fireclay insulators; on the experimental arm these insulators were 3 in. long, but 12-in. lengths are used in the improved design. The insulators (with wires threaded) are housed in a $\frac{1}{2}$ -in. dia. mild-steel gas tube, which is inserted in the $\frac{13}{16}$ -in. dia. main tube and retained in position by a set-screw. The insulator nearest the head is held in position by a small fibre wedge and, as a further precaution against the insulators slipping or putting a strain on the wires, the $\frac{1}{2}$ -in. dia. tube is slightly nipped together at the other end. The hot-junction end is completed by a narrow twin-bore fireclay insulator and a good twisted junction of the wires is made, leaving about $1\frac{1}{2}$ in. bare at this end.

The opposite end of the arm terminates in a head assembly consisting of an "Amalgams" base-metal couple head stripped of its terminals. This assembly is held in position by a collar and set-screws and houses the spools for a reserve supply of couple wire, together with a "jack" socket. The brass spools are insulated from each other by felt washers and from the metal head by a fibre $\frac{1}{4}$ -in. Whitworth bolt. The felt washers act as light springs; by a gentle pull from the hot-junction end the wire can therefore be drawn through when renewing the hot junction. Sufficient pressure is exerted by these washers to maintain a positive contact with copper washers extended to the "jack" socket. The small length of wire between the last fireclay insulator and the spool at this end is insulated by small-bore Systoflex. The ends of the couple wires are soft-soldered to the spools before winding, and a careful twisted connection is made when a new reserve of wire is attached. Full spools are held ready for

insertion when the reserve on the instrument is exhausted. The whole inner tube is retractable, and in case of necessity a complete new internal assembly can be inserted in a few minutes. The hot junction is protected by a silica sheath, 4 in. long and of 6-mm. bore, the sheath being renewed after each immersion.

For ease of renewal of this sheath a simple device has been adopted. A tapered plug (1 in. long and $\frac{3}{4}$ in. $-\frac{7}{8}$ in. in dia.) of plumbago and "Sair-set" cement is moulded round the silica sheath by means of a suitably split brass mould. The plug when dry effectively grips the sheath and is manually inserted in the $\frac{3}{4}$ -in. hole in the last graphite sleeve. A slight twist then makes an effective seal.

The total weight of the couple arm, when fully assembled, is about 20 lb.

For manipulation the arm is attached to a light jib arrangement (see Fig. 1). This jib is mounted on hinges attached to the back-wall furnace binding nearest the middle line of the furnace; it is at a minimum safe height above the bath bank level. When not in use the whole apparatus swings back parallel to the furnace back wall.

The thermocouple arm is suspended by light wire ropes on pulleys running down a rail and runs over a fixed pulley at the bottom end. For an immersion, the jib is swung into position and the arm runs by its own weight down the rail and through a suitable hole in the back wall at a predetermined angle of 30° . On the furnaces at the Templeborough melting shop this angle gives, with the length of arm stated, a similar depth of immersion (9 in.) into the steel to that obtained with the trolley apparatus. The horizontal location is approximately half-way between the middle line of the furnace and the back bank.

Two pairs of rollers are used to suspend the arm on the rail to give the requisite rigidity. Any tendency to sag when inserted in the bath is compensated by the buoyancy of the slag and metal. Various devices (some semi-automatic) have been tried for retracting the arm from the furnace. In the final design a small hand-winch with a steel wire rope over pulleys is incorporated for easy withdrawal of the arm. A counter-balance weight is attached to the drum of the winch. The whole operation is very simple, and is easily carried out by one person.

Experience with the new type of arm has given complete satisfaction. Its maintenance, both in time and cost, is small. The plumbago sleeves will give about 200 immersions before renewal, and the other parts of the assembly have an indefinitely long life.

The whole arm can readily be removed and replaced at any time. Being on the back wall of the furnace it is out of the way of chargers, locomotives, &c., and does not impede furnace

operations. Another advantage is that the apparatus permits attachment of the instrument to indicators or recorders.

The instrument should prove readily adaptable to most types of open-hearth furnaces, and to many electric furnaces. For use with sloping walls a longer arm would be required or, alternatively, the arm could be inserted through the angle between the sloping and the straight portions of the wall. Trials on this type of wall are to be made as and when opportunity permits.

Steel End Block.

The original design of arm for all types of immersion thermocouples had an end block of diatomaceous material to protect the end from liquid steel and slag. Blocks of this type were quickly eroded by basic slag and were soon superseded by end blocks of graphite,⁴ which were impervious to acid or basic slags and had an exceptionally long life. The graphite end block has been universally adopted and was an outstanding development in design. It has been suggested, however, that the carbon block may have had a bearing upon the embrittlement, which is experienced periodically, of the couple wires. A similar type of end block made from mild steel was therefore tried and was immediately successful, both with acid and with basic slags.

On dipping through the slag a coating adheres to the steel block, protecting it from attack by the liquid steel for a period which gives ample time to take a temperature reading. The blocks have an indefinitely long life; one block recently examined had been used 750 times with little or no visible effect, there being practically no signs of attack by the liquid steel. After the first few immersions there appears to be slight distortion of the threads, and the blocks are removed and re-threaded, after which no further trouble ensues.

In order to test the effect of the steel block on the actual temperature readings a series of readings were taken, consecutive and simultaneous dips being made with a carbon end block and a steel one. In no case was there any significant discrepancy in the two readings, the greatest difference being of the order of $\pm 3^{\circ}\text{C}$. In consequence of these satisfactory tests all of the appropriate instruments on the plant have been

fitted with steel end blocks, which have been in regular use for some months.

The most striking feature of the use of the steel end blocks has been the total disappearance of embrittlement of the rare-metal couple wires; not a single instance of this has been encountered in the period during which this type of block has been in use. Evidently the carbon monoxide resulting from immersion of the carbon end blocks had been a contributory factor in the embrittlement troubles previously experienced.

Further Suggested Improvements.

As a result of the success of the steel end blocks a back-wall pyrometer arm constructed from a hollow steel bar with no outer insulation is in the course of preparation. The additional weight of the arm will be little or no disadvantage with this type of installation, as the whole of the weight is taken by the jib and the arm is mechanically retracted after use.

A further instrument is to be constructed with a steel end block sufficiently long to protect the end which is immersed in slag and metal and having plumbago sleeving to protect that portion of the arm which is exposed to the furnace flame.

CONCLUSION.

The new type of arm and end block have helped to simplify the operation of temperature measurement, have considerably cut down maintenance, and have reduced embrittlement troubles.

ACKNOWLEDGMENTS.

The authors desire to thank the management of Messrs. Steel, Peech and Tozer for permission to publish this paper, and also their colleagues for their co-operation.

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AN EXPERIMENTAL ENQUIRY INTO THE INTER-ACTIONS OF GASES AND ORE IN THE BLAST-FURNACE.

PART VI.—INFLUENCE OF LIMESTONE ON THE REDUCTION OF IRON ORE AT UP TO 850° C.*

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SYNOPSIS.

The effect of limestone (and lime) on the reduction of iron ore by blast-furnace gas is examined under conditions where no interaction occurs between the solids. The temperature range covered is 450–850° C.; equilibrium conditions and reaction velocities are both studied.

At 450–550° C., limestone behaves as a diluent; the same is true concerning lime at 850° C. Lime, however, by absorbing CO₂, accelerates carbon deposition at low temperatures.

Up to 750° C., ore reduction predominates and eventually reverses limestone decomposition; at 850° C., limestone decomposition reverses ore deoxidation. At 750° and 850° C. these changes occur when the gas contains about 10% of CO₂.

The rates of ore reduction measured at corresponding temperatures and CO₂ concentrations are not appreciably altered by the addition of limestone to the ore.

I.—INTRODUCTION.

IN previous work on the reduction of iron ore by blast-furnace gas† (this series of papers, Parts I.,¹ II.,² III.,³ IV.,⁴ and V.⁵) particular attention was paid to the influence of temperature, CO/CO₂ ratio, speed of gas flow, and the addition of small quantities of hydrogen and steam. The important part which limestone plays in normal smelting practice suggested the extension of the research to systems which included that substance, though observations have been restricted to pre-slagging temperatures (450–850° C.). The materials used were a West Coast hematite (ore A of previous researches) and Rowrah limestone, and experimental conditions were so arranged that they did not diverge too widely from blast-furnace conditions.

Limestone decomposition occurs at temperatures where ore reduction is rapid, and the value of the CO/CO₂ ratio at any instant depends upon changes occurring both in the ore and in the stone. In practice, before the decomposition temperature is reached, all the materials have to pass through the top of the stack; any changes in this region must therefore be taken into consideration. A wide range of CaCO₃→CaO decomposition was

studied, because segregation and unequal descent may cause variations in the carbonate/oxide ratio; this would mean that different portions of the charge reach a particular temperature zone in different states of preparation. Moreover, lime has occasionally been added in place of limestone to meet the burden requirements.

Other carbonates likely to enter the furnace are MgCO₃ (as magnesian limestone or dolomite) and perhaps MnCO₃ and FeCO₃ (uncalcined spathic ore); these are progressively easier to decompose, decomposition pressures of 1 atm. being attained at about 900° C. for CaCO₃ and below 550° C. for MgCO₃, while it was found that precipitated FeCO₃ decomposes between 100° and 200° C., giving CO₂ which at 270° C. oxidizes the solid, with formation of CO.

Lime and magnesia may interfere with the reduction of iron oxides below 1000° C., under certain conditions (fine sub-division, long heating, and excess of alkaline earth). Schenk and colleagues,⁶ showed that a mixture of calcium or magnesium and ferric oxides prepared from mixed nitrates by ignition gave different equilibrium values from the pure oxide. A similar divergence was noted in the following extreme

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† "Blast-furnace gas" is used to indicate a synthetic blast-furnace gas, the initial composition of which is 33.3% of carbonic oxide and 66.7% of nitrogen (by volume).

case, using partly deoxidized $\frac{1}{40}$ -in.- $\frac{1}{60}$ -in. ore *A* and magnesia powder :

	MgO/Fe ₂ O ₃ (molecular ratio).	Heating, time and temp.	Equilibrium CO/CO ₂ (at 800° C.).
Ore <i>A</i> and magnesia powder	0.7	24 hr. at 800° C.	1.9 (50% deoxidation).
	2.0	1 week at 800–900° C.	3.0 (70% deoxidation, no carbon deposition).
Ore <i>A</i> alone			1.9 (FeO-Fe).

In the present investigation, where there were no fines below $\frac{1}{10}$ -in. mesh or preheating other than raising to the experimental temperature (850° C. maximum) and always an excess of ore, no fluxing or interpenetration of the solids was observed.

The rate of ore reduction in a rapid stream of hydrogen at 750° C. with a $\frac{1}{4}$ - $\frac{1}{10}$ -in. mesh mixture of ore *A* and twice its bulk of lime (free from limestone) was only slightly altered after submitting the mixture to an initial preheating of 66 hr. at 700–950° C. (including 13.5 hr. at 950° C.); such conditions were far more stringent than any occurring in a normal experiment.

As the experimental charge consisted of a mixture of lumps of different material instead of ore alone, it becomes necessary to qualify the con-

same as those already described in earlier papers of this series (*loc. cit.*). A closed-circuit system was employed, comprising circulating pump, reaction tube, CaCl₂ drying-tube, capacity vessel, sampler, and manometers. In order to prevent premature decomposition of the limestone, the reaction tube was fitted with a special gas-tight feed (Fig. 1) within the circuit; by means of this arrangement weighed amounts of dried stone and/or calcined or partly deoxidized ore could be introduced as required into the vertically mounted reaction tube, the heating current being temporarily increased to counteract cooling.

The changes in composition of the different solid materials and the gas were followed by taking pressure readings and simultaneous gas samples for subsequent analysis; mercury additions were made to compensate for the gas removed.

III.—DISCUSSION OF RESULTS.

(a) General.

Preliminary work was devoted to the decomposition of the Rowrah limestone alone under varying conditions. Equilibrium pressures measured at 650°, 750°, 850°, and 900° C. agreed closely with Johnston's figures,⁷ which are shown in Fig. 2 (curve 1) plotted (in mm. Hg) on a logarithmic

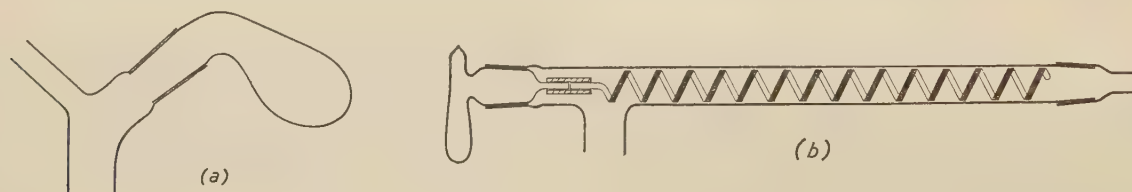


FIG. 1.—Gas-tight Feeding Apparatus: (a) Rotary joint for bulk charging; (b) helix for intermittent charging.

cept of contact time, because, if it is implied that the gas takes proportionately longer to traverse the mixture than it would either of the components separately, a distinction must be made between time of contact with the whole charge and the time of contact with the ore, the latter being the basis adopted.

II.—EXPERIMENTAL METHOD.

The materials had the following compositions :

	Fe ₂ O ₃ , %.	CaO, %.	Al ₂ O ₃ , %.	SiO ₂ , %.	CO ₂ , %.	H ₂ O, %.
West Coast hematite.	82.4	0.9	0.2	14.6	—	0.6
Rowrah limestone	0.3	55.2	0.1	0.4	42.9	0.1

The ore and stone were crushed and sized between $\frac{1}{4}$ in. and $\frac{1}{10}$ in., and were usually employed in the ratio of 5 : 1 (ore : stone, by weight).

It is not necessary to describe the apparatus and procedure in detail, as they were substantially the

scale against temperature (° C.). As the CO₂ pressure increases, the stable solid phase changes from lime (on the right of curve 1) to limestone (on the left). Some of the data useful for future reference are :

Temperature, ° C. :	650.	750.	850.	900.
Equilibrium pressure, mm. Hg	8	68	373	773
Equilibrium pressure, atm.	0.01	0.1	0.5	1.0

To keep the (CO + CO₂) pressure at $\frac{1}{3}$ atm., the CO₂ pressure cannot exceed 253 mm.

Though equilibrium CO₂ values are independent of the nature of the calcium carbonate, it was found that its rate of decomposition may vary considerably according to its physical condition, *e.g.*, CaCO₃ re-formed from decomposed stone and carbon dioxide decomposes at a greater rate than the original stone; again "chalky" limestone and fines both decompose more readily than "spar" stone or lumps. The rate is likewise

influenced by the ambient gas, being lowered by increasing pressure. At 740°C . the rate of recombination of lime and CO_2 in an atmosphere with CO_2 content equal to twice the dissociation pressure of CO_2 is of the same order as the decomposition rate of the original stone.

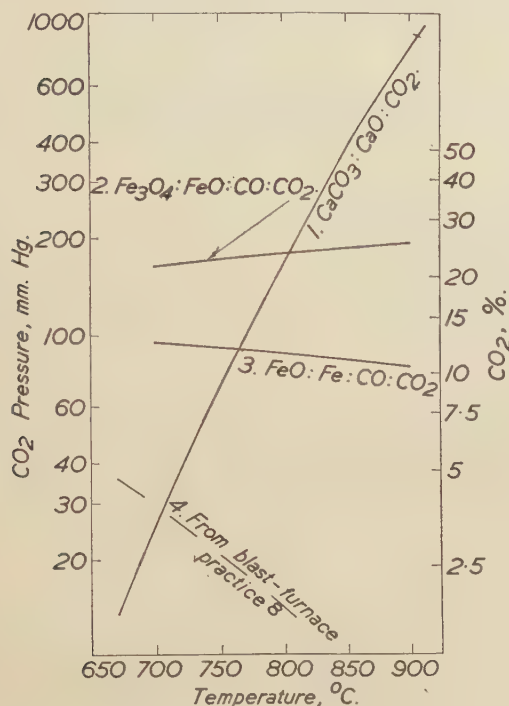


FIG. 2.— CO_2 Pressure Curves.

Curves for CO_2 pressure (and percentage in 1 atm. of gas) are given in Fig. 2 for the following equilibria:

$\text{Fe}_3\text{O}_4 : \text{FeO} : \text{CO} : \text{CO}_2$; curve 2.
 $\text{FeO} : \text{Fe} : \text{CO} : \text{CO}_2$; curve 3.

Both are deduced for a $\text{CO} + \text{CO}_2$ pressure of $\frac{1}{3}$ atm., from the ratios already ascertained for ore A. As the CO_2 pressure diminishes, the stable solid phase changes from Fe_3O_4 above curve 2 through FeO (wüstite) between curves 2 and 3 to Fe (oxyferrite) below curve 3. It will be seen from the slopes of the respective curves that changes in temperature affect curve 1 to a much greater degree than they do curves 2 or 3; the intersections of curve 1 with curves 2 and 3 give the conditions under which four solid phases can exist in equilibrium with gas, viz.:

Equilibrium	CO_2 Pressure (mm. Hg.)	Temp., $^{\circ}\text{C}$.
$\text{Fe}_3\text{O}_4 : \text{FeO} : \text{CaCO}_3 : \text{CaO}$	182	805
$\text{FeO} : \text{Fe} : \text{CaCO}_3 : \text{CaO}$	91	765

If either the CO_2 pressure or the temperature be altered, one of the solid phases disappears. It should be noted that the introduction of a fifth

solid phase, carbon, to the above four-component systems does not permit of any equilibrium at all.

The relevant conditions in the blast-furnace are shown in curve 4, which was plotted from data derived from a report⁸ of English blast-furnace practice, taking the pressure in the shaft as 1 atm. In view of the disturbed conditions and sudden changes which occur in the furnace, curve 4 is a rough guide only, but the rapid fall in CO_2 with increasing furnace temperature, coupled with the rapid increase in the limestone decomposition pressure, indicates that there is a fairly sharp demarcation between the zones of limestone stability and of limestone decomposition (the latter being inappreciable below the point of intersection of curves 1 and 4, circa 700°C .). In American practice⁹ the CO_2 in the shaft may exceed that represented in curve 4, the region of limestone stability being correspondingly extended.

The removal of CO_2 by coke ($\text{C} + \text{CO}_2 = 2\text{CO}$) was much slower than either ore reduction or limestone decomposition, the CO_2 produced in a matter of seconds requiring a contact time of minutes for reconversion to CO . This illustrates the importance of contact time, for if this time were so extended that equilibrium conditions were approached, a slow reaction could become a major controlling factor. In the blast-furnace the CO/CO_2 ratio is not generally low enough below 750°C . to permit carbon solution.

It would seem advisable to eliminate the CO_2 from the limestone at as low a temperature as possible; the CO_2 would then cause the minimum retardation in the rate of oxygen removal from the ore. In this connection the use of dolomite is interesting, in that magnesium carbonate decomposes earlier than calcium carbonate, likewise carbonate re-formed from lime and CO_2 decomposes faster than normal stone.

The separate equilibrium values for ore/gas and limestone/gas remain unchanged when the ore and stone are mixed together. In the latter case CO_2 accumulates from both of the reactions, and the equilibrium CO_2 pressure is reached more quickly, though each separate reaction contributes less CO_2 in a given time.

Reaction velocities should be compared at the same CO_2 concentration, irrespective of contact times. Under these conditions the rates of ore reduction, based on contact time with ore, at corresponding temperatures and states of de-oxidation remain practically unchanged when the ore is mixed with limestone.

In certain circumstances the CO_2 content may rise to a value in excess of that for one of the equilibria and the ore is oxidized, or CaCO_3 re-formed, just as would happen if the composition of the gas were controlled artificially instead of by the reaction with the greater CO_2 pressure. In the case of carbon deposition at

450° C., limestone remains inert; lime behaves similarly towards ore reduction at 850°. In these circumstances the lime and the limestone are merely solid diluents.

(b) *Results for Particular Temperatures.*

(i) **At 450° C.**

Previous work has shown that there is only a relatively small amount of reduction at this temperature and only a short time elapses before the deposition of carbon assumes priority; addition of limestone to the ore only influences this reaction as a diluent.

When, however, the calcium addition is made as lime, this combines with CO_2 , and carbon deposition is considerably accelerated, some oxygen being eliminated concurrently. This is a normal result of decreasing the CO_2 content of the gas, as was shown in other experiments where gas composition was altered in absence of lime. Both of the reactions $2\text{CO} = \text{C} + \text{CO}_2 + 41 \text{ kg. cal.}$ and $\text{CaO} + \text{CO}_2 = \text{CaCO}_3 + 42 \text{ kg. cal.}$ are exothermic; additional heat (though less than that required to burn the limestone externally) would therefore be generated in the top portion of the stack, thus altering the normal temperature gradients in this region. Furthermore, the top gas would have a higher calorific value.

Even if all the calcium oxide were converted to carbonate, the disintegration produced by the rapidity of the reaction in its early stages would render the ore much more permeable to the reducing gas, and reduction would continue at a scarcely diminished rate. This result is important because not only may the reduction of the ore be extended at a relatively low temperature by such disruption, but the additional carbon may favourably influence the reaction over a greater temperature range than that where impregnation and deposition normally occur. It has already been shown² (*loc. cit.*, p. 50), that, at 750° C., reduction by solid carbon may be appreciably greater than that by blast-furnace gas of normal CO_2 content.

One disadvantage of substituting lime for limestone lies in its lower mechanical strength, resulting in an increase of fines; another is that earlier slagging of the powdered materials might, in some circumstances, prejudice reduction.

(ii) **At 700–750° C.** (CaCO_3 decomposition pressure = 25–68 mm.).

At 700° C. limestone decomposition is relatively slow, unless much hydrogen is present. At temperatures between 700° and 750° C. limestone decomposition and ore reduction proceed simultaneously (the latter being the faster) until the CO_2 content of the gas reaches the decomposition pressure of the limestone. At this point the

corresponding CO/CO_2 ratio is still above the equilibrium value for the iron oxide systems and so reduction of the ore continues and some of the lime is reconverted into carbonate, *i.e.*, the total carbon in the gas reaches a maximum and then decreases. Thus, between 700° and 750° C., ore reduction predominates and imposes its own equilibrium on that of the system.

(iii) **At 750° C.** [CaCO_3 decomposition pressure = 68 mm.; equilibrium pressure of CO_2 ($\text{CO} + \text{CO}_2 = \frac{1}{2} \text{ atm.}$) = 92 mm. for the reaction $\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$].

At 750° C. the rate of limestone decomposition varies considerably with the nature of the stone and other conditions (*see* p. 68 P) but is still comparatively slow. The partial pressure of CO_2 at equilibrium is, however, always less than that for ore deoxidation when carbon deposition is absent.

The general course of the reaction at 750° C. between blast-furnace gas at atmospheric pressure and a charge of limestone and ore (up to some 70% reduction) is illustrated in Fig. 3, where the

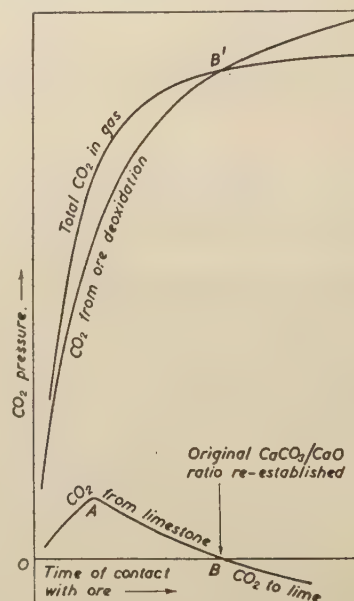


FIG. 3.—Ore A, Limestone, and Blast-Furnace Gas at 750° C.

separate pressures of CO_2 from ore deoxidation and from limestone decomposition, and their sum (*i.e.*, total CO_2 in the gas) are plotted against time of contact with the ore. Although the total CO_2 in the gas gradually increases throughout an experiment, the relative amounts contributed by the two reactions vary continuously, and a critical point (A, Fig. 3; total $\text{CO}_2 = 9\%$) is soon reached when the CO_2 from the limestone reaches a maximum. So far the limestone has suffered decomposition, but once this decomposi-

tion pressure is exceeded ore reduction continues and any excess of CO_2 combines with lime, reforming carbonate. Provided that some free lime were present at the start, recombination continues until the point (*B*, Fig. 3) is reached when the initial CaCO_3/CaO ratio is re-established. Beyond this point reduction of ore still occurs, but the actual carbon content of the gas decreases further so long as lime remains.

In the absence of free lime at the start, the two upper curves approach one another, and the time axis becomes the asymptote of *AB*. If lime (free from carbonate) be initially present, then the two upper curves approximately coincide and the lower curve follows the time axis until the decomposition pressure of the carbonate is reached. When the decomposition pressure is exceeded, CO_2 combines with lime and the curves diverge, as at the right of *B'* and *B*.

At lower or higher ore deoxidations than those shown in Fig. 3, the " CO_2 from limestone" curve lies respectively below or above curve *OAB*. The point *A* is reached at a contact time which is less than one second for virgin ore, this time extending to a matter of seconds when deoxidation approaches the stage of carbon deposition. Before reduction reaches the wüstite stage, CO_2 from limestone decomposition is only a fraction of that arising from ore deoxidation. To the left of *B* the extra CO_2 (from the limestone) in the gas suppresses the reduction a little below what it would otherwise be if no limestone were present, but to the right of *B* the removal of CO_2 encourages both deoxidation and carbon deposition.

As the degree of reduction increases, point *B* (corresponding with contact times of several seconds) moves to the right until the time-interval *OB* is too long to have any significance in the blast-furnace, where the contact time in the 750°C . zone is only a fraction of a second. In practice, at the temperature being considered, the amount of carbonate decomposed (or formed) depends upon the CO/CO_2 ratio of the gas entering the zone and on the changes in composition already suffered by the ore and stone.

(iv) At about 785°C .

At this temperature the decomposition pressure of the limestone (curve 1, Fig. 2) lies between the CO_2 pressures for the two deoxidation equilibria, $\text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2$ (curve 2) and $\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$ (curve 3). From curve 2 to curve 3 the equilibrium CO_2 pressure for the ore/gas system alone falls continuously and rapidly as ore deoxidation increases from about 25% (*i.e.*, disappearance of Fe_3O_4) to about 30% (*i.e.*, appearance of iron (oxyferrite)); within this range of reduction one iron phase only (wüstite) exists in equilibrium with the gas; if lime or limestone be present three phases may coexist in

equilibrium with the gas at temperatures near 785°C . Outside this range the appearance of a second iron phase renders the system unstable, and one of the calcium phases (lime at 750°C . and limestone at 850°C .) must disappear before a new equilibrium can be established.

(v) At 850°C . [CaCO_3 decomposition pressure = 373 mm.; equilibrium pressure of CO_2 ($\text{CO} + \text{CO}_2 = \frac{1}{3}\text{ atm.}$) = 84 mm. for the reaction $\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$].

At this temperature the decomposition of limestone is much more rapid and is roughly proportional to the amount of limestone present. The decomposition pressure for CaCO_3/CaO at equilibrium is far in excess of the requirements for the ore-reduction equilibria, and the total ($\text{CO} + \text{CO}_2$) pressure increases continuously, without any maximum (*cf.* 750°); adjustments were thus sometimes necessary in the experiments to maintain the correct total pressure and the diluent value of the nitrogen.

At the start of the reduction the CO_2 from deoxidation of the partly reduced ore may be formed as fast as that from the partly decomposed limestone, but the total pressure of CO_2 soon exceeds that for the CO/CO_2 equilibrium ratio, and the ore is reoxidized. Fig. 4 shows the

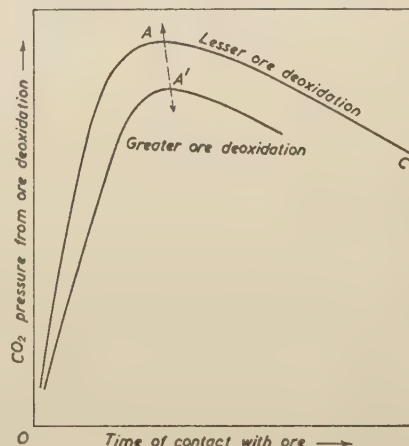


FIG. 4.—Ore A, Limestone, and Blast-Furnace Gas at 850°C .

pressure of CO_2 from ore deoxidation at *circa* 35% plotted against time of contact with the ore. At the reduction-oxidation transition point, *A*, the CO_2 in the gas equals that for the ore-deoxidation equilibrium, *viz.*, 11%. With slightly decomposed stone point *A* occurs at less than one second of contact with the ore. The position of point *A* depends upon the degree of reduction of the ore, the amount of undecomposed carbonate and, if they have altered, the ($\text{CO} + \text{CO}_2$) and N_2 pressures. The downward slope to the right of *A* and *A'* indicates that oxidation is occurring,

and this continues until all the limestone is decomposed.

The lower curve relates to ore of a slightly greater deoxidation. As reduction increases, OA' becomes less steep, the rate of deoxidation being slower and the CO_2 from the limestone making a greater contribution to the total CO_2 present. AA' is inclined away from the CO_2 pressure axis.

The foregoing results and discussions show that the reactions taking place at any instant vary with temperature, CO_2 concentration, time of contact, and pretreatment; these reactions, although somewhat complex, are capable of separate analysis and assessment by the experimental method employed. The changes in the character of the reactions with increasing contact times are particularly interesting and, when it becomes possible to define the limits of the various temperature zones and corresponding CO_2 concentrations of the gas in the blast-furnace with greater accuracy, the data now available will facilitate a fuller interpretation of ironmaking practice.

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DISTRIBUTION IN THE GAS PRODUCER.*

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(Figs. 5 to 42 = Plates V. to VIII.)

SYNOPSIS.

The problem of distribution in the gas producer is studied, with the aid of small-scale sectional models, from two complementary aspects, namely, the segregation of the fuel and the distribution of the air blast.

The segregation of the fuel was recorded photographically and was also analysed by dividing the model producer into vertical compartments by means of metal strips introduced from the back. The effects of various modifications of materials and of producer design were examined, and methods of segregation control are described.

The air blast associated with various types of solid segregation were examined qualitatively and assessed quantitatively by measuring the pressure drop between various points across the bottom of the bed and the atmosphere.

A special technique was devised to determine the extent and location of the ash-bed.

Some preliminary experiments on the combustion of coal in a simple model producer are described.

I.—INTRODUCTION.

THE problem of distribution in the gas producer is in many respects similar to that of distribution in the blast-furnace, though in the gas producer the question is somewhat simplified by the fact that the burden is limited to one class of material. Whereas, however, in modern blast-furnace practice there has been a definite trend towards the exercise of greater control in the selection of the raw materials, it can hardly be said that similar care is as yet generally taken in the preparation of the fuel for gas producers. Gas-producer design varies considerably, from the simple static type to the more modern mechanically operated and controlled machines with their special levelling and agitating devices, but the problems of the fuel bed and its distribution are common to all; for wherever there is segregation there will be channelling, with inequality of gas flow and variation of time of contact through parts of the bed, which will lead to local changes in the composition of the gas and an overall reduction in efficiency.

In all this work the two complementary aspects of the problem have been under consideration, *viz.*, segregation in the fuel and distribution of the gas.

Experimental Method.

Small-scale models ($\frac{1}{24}$ th linear) were again employed, as in the corresponding investigation relating to blast-furnaces.† These models were

generally of the "slice" type, *i.e.*, representing a vertical section through the centre of the producer; similar experiments performed in semi- and fully circular models showed that the slice technique was satisfactory. In special cases an allowance was made for differences in the volumes represented by the central and peripheral regions respectively. The static producer, being the simplest, proved the most suitable starting-point and in the present investigation the experimental work was restricted to models of this type of producer.

The models were constructed of wood, with a glass face to permit visual observation and photographic recording. The depth of the bed and the location of its surface could be controlled by means of a piston sliding in a well below the grate. The charging system consisted of a miniature bell and hopper, attached to a top plate and adjustable vertically, while the materials employed were sized between specified limits (again to scale). In all cases where it was desired to analyse the segregation, a plywood back plate slotted vertically over rather more than half its width to accommodate thin metal strips was employed; the metal strips were adjusted with the inside back surface of the model at the commencement of each segregation experiment. (See Fig. 1.)

The body of the model was first charged to the apex level of the grate with a horizontal layer of any suitable material which could later be readily separated from the bed under investigation. The

* Received December 21, 1945.

† Saunders and Wild, *Journal of The Iron and Steel Institute*, 1945, No. II., pp. 259 P-286 P.

top plate was then set at the requisite height and a standard volume of coal added. In order to maintain a constant depth of fall, the top plate was raised by an amount equal to the thickness of the coal charged, this procedure being continued until the plate had been raised to its normal position. At this stage the metal strips were pushed forward until they touched the glass, thus

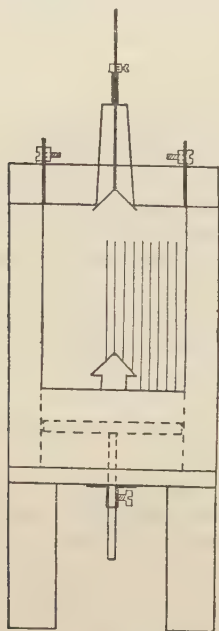


FIG. 1.—Model for Distribution Experiments.

dividing one side of the bed into sections of equal width. The model was then turned on its back, the front glass and top plate removed, and a slotted metal strip inserted horizontally immediately over the apex of the grate. The contents of each compartment above this level were then brushed out and submitted to sieve analysis.

For the purpose of making photographic records it was desirable to use materials of contrasting colour, and it was demonstrated that this could be satisfactorily accomplished by the use of white and dyed marble in place of coal. That this technique introduced no appreciable change in the distribution characteristics may be seen from an examination of Fig. 2(a), which illustrates the results of experiments performed under identical conditions except that the burden was in one case coal and in the other marble (of contrasting colours).

It will be appreciated that, in practice, the grading quality of the fuel varies over a wide range according to the particular characteristics of the coal employed. To use similarly scaled material throughout the whole of this investigation would have necessitated much labour in

preparation of the charges and in their subsequent size analysis. Moreover, such complex gradings tend to mask the effects caused by changes in design or operation. The simplest mixture is one of two components only, and this, as will be seen from the following experiments, gives a very good picture of the overall effect of size variation. In any mixture charged the fines tend to accu-

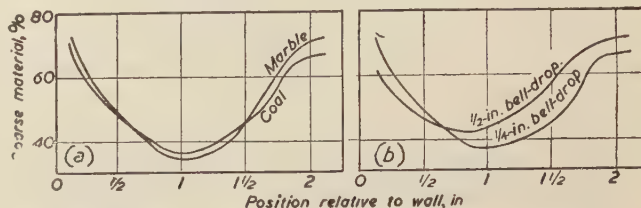


FIG. 2.—Distribution : (a) Comparison of distribution of coal and marble ; (b) influence of bell-drop variation.

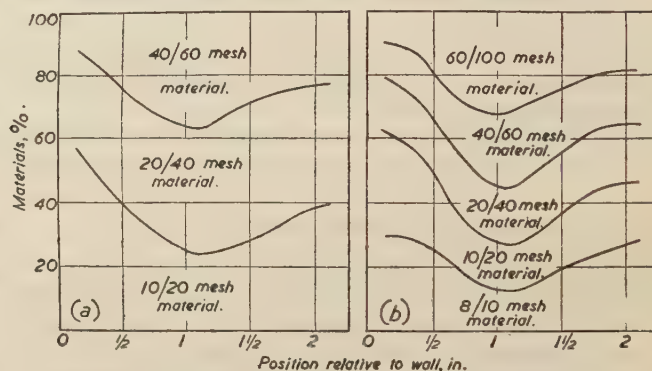


FIG. 3.—Distribution. Behaviour of uniform gradings : (a) Three-component mixture ; (b) five-component mixture.

mulate near their point of impact, while the larger particles roll in the troughs.

Two experiments with uniform gradings, the first with size variation of 1:6 and the second 1:12, demonstrate this point. In the first case the

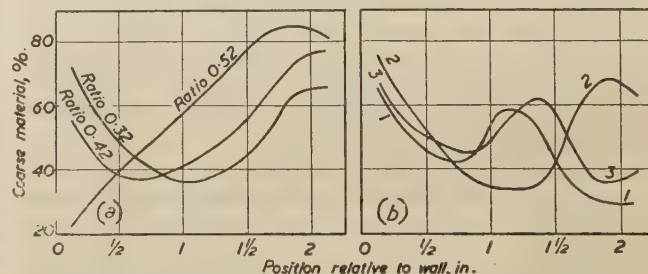


FIG. 4.—Distribution : (a) Influence of variations in bell/body ratio ; (b) influence of central charging through apertures closed by rising plug (curve 1), dropping bell (curve 2), and dropping bell with funnel (curve 3).

mixture was separated into three components (10/20, 20/40, and 40/60 mesh material) and in the second was treated as a mixture of five components (8/10, 10/20, 20/40, 40/60, and 60/100 mesh material). It can be seen from Fig. 3 that

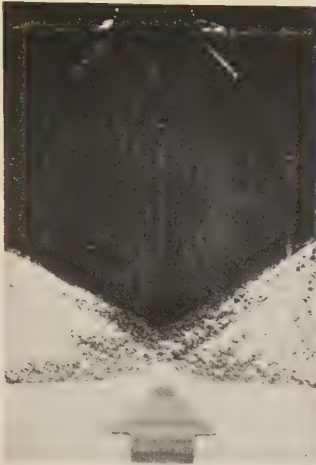


FIG. 5.—Bell/Body Ratio, 0.52.



FIG. 6.—Bell/Body Ratio, 0.32.
Zero discharge.



FIG. 7.—Half Discharge.



FIG. 8.—Full Discharge.

FIGS. 5 and 6.—Influence of Variation in Bell/Body Ratio upon Distribution. (See also Fig. 4(a).)

FIGS. 6 to 8.—Influence of Discharge upon Grate Conditions. (See also Fig. 43(a).)



FIG. 9.—Flow Lines: First stage.



FIG. 10.—Flow Lines: Second stage.

FIGS. 9 and 10.—Influence of Grate Conditions upon Flow Lines.

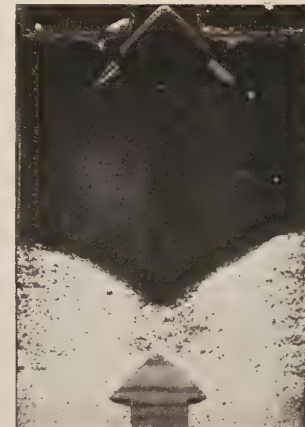


FIG. 11.—Ring/Body Ratio, 0.48.



FIG. 12.—Ring/Body Ratio, 0.65.

FIGS. 11 and 12.—Influence of Deflector-Ring Dimensions upon Distribution. (See also Fig. 45(a).)



FIG. 13.—Aperture Closed by Rising Plug.



FIG. 14.—Aperture Closed by Diminutive Bell.



FIG. 15.—Aperture Closed by Diminutive Bell, with Funnel.

FIGS. 13 to 15.—Influence of Central Charging through apertures closed by different methods upon distribution. (See also Fig. 4(b).)

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FIG. 16.



FIG. 17.

FIGS. 16 and 17.—Air Flow through Uniform Burden; standard grate.



FIG. 18.

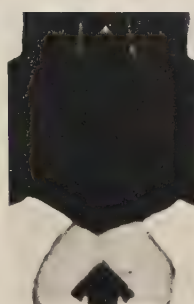


FIG. 19.

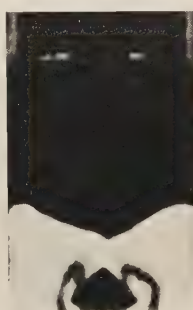


FIG. 20.



FIG. 21.



FIG. 22.



FIG. 23.

FIGS. 18 to 23.—Air Flow under Various Conditions : Figs. 18 and 19, mixed burden charged from normal bell (see Fig. 44(a)); Figs. 20 and 21, mixed burden charged from normal bell with deflector ring (see Fig. 44(b)); Figs. 22 and 23, mixed burden charged from normal bell, with head-gear as in Fig. 44(d)).



FIG. 24.

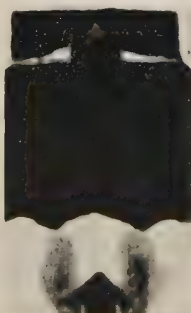


FIG. 25.



FIG. 26.



FIG. 27.



FIG. 28.

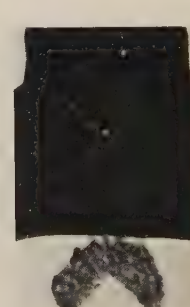


FIG. 29.

FIGS. 24 to 29.—Air Flow under Various Conditions : Figs. 24 and 25, mixed burden charged from normal bell, with head-gear as illustrated in Fig. 44(c); Figs. 26 and 27, mixed burden charged from normal bell, with head-gear as illustrated in Fig. 44(e); Figs. 28 and 29, uniform burden and slotted grate.

FIGS. 16 to 29.—Air Flow under Various Conditions.



FIG. 30.



FIG. 31.



FIG. 32.



FIG. 33.



FIG. 34.



FIG. 35.



FIG. 36.

FIGS. 30 TO 36.—Ash-Bed Formation: "Fuel" containing 25% of "ash."



FIG. 37.



FIG. 38.



FIG. 39.

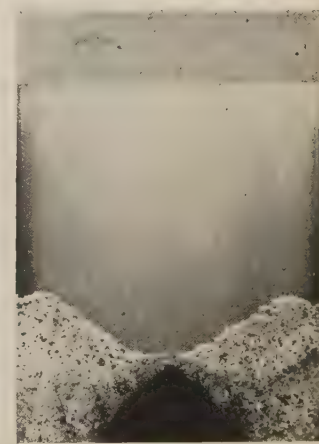


FIG. 40.

FIGS. 37 AND 38.—Ash-Bed Formation: "Fuel" containing 15% of "ash." FIGS. 39 AND 40.—Ash-Bed Formation: "Fuel" containing 5% of "ash."

FIGS. 30 TO 40.—Stages in Ash-Bed Formation, with "fuels" of various "ash" contents.



FIG. 41.—Corrected Distribution with Deflector Ring and Central Charging.

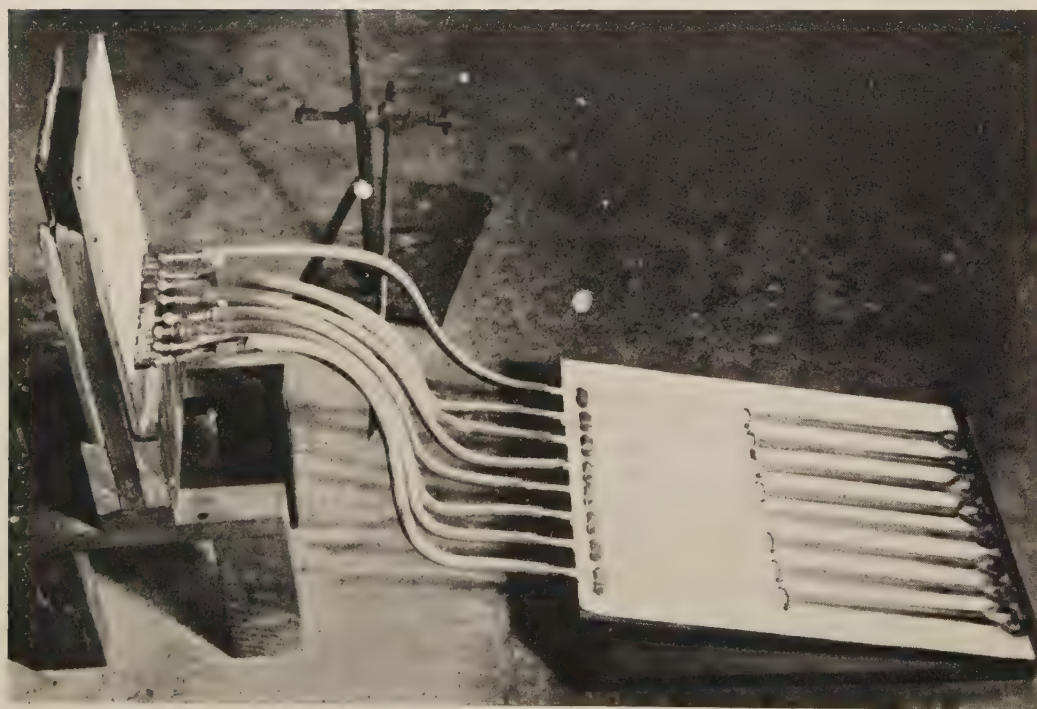


FIG. 42.—General Arrangement of Apparatus for Measuring Pressure Differences.

the respective segregations of fine and coarse material are similar to those obtained with a two-component mixture. In Fig. 3(b) it will be noted that the distribution patterns for both of the groups 8/10, 10/20 and 40/60, 60/100 mesh are similar in character.

II.—IMPORTANT FACTORS INFLUENCING FUEL DISTRIBUTION.

(a) *Effect of Varying Bell-Drop.*

The normal scaled bell-drop was $\frac{1}{4}$ in. When this was doubled the bed surface was somewhat flattened, with a consequent decrease in segregation (see Fig. 2(b)); this effect is mainly a result of the increased velocity of the material at the region of impact, which tends to lower the repose angle and so lessens the rolling tendencies. It can also be seen that the region of maximum fines moves nearer the walls and that the excess of coarse material which exists there under normal bell-drop conditions is reduced. In this respect such distribution resembles, but in lesser degree, the behaviour of chute-charged materials, though in the latter case the velocity increase can be sufficient to change the bed surface to such an extent that the distribution pattern is entirely altered.

(b) *Effect of Varying Bell/Body Ratio.*

A similar result to that described for increasing bell-drop is obtained by increasing the bell/body ratio. The normal bell/body ratio was 0.32. As this ratio was increased the region of maximum fines moved towards the wall, which is reached at a bell/body ratio value of 0.5; meanwhile the quantity of coarse material at the centre increases. (Figs. 4(a), 5, and 6.)

(c) *Effect of Varying Bed-Surface Height.*

For the normal bell/body ratio of 0.32 the trajectory of the falling material is such that the point of impact with the wall lies below the normal bed-surface level; hence, in these circumstances, the region where fines predominate is situated on the centre side of the stream, since the fine material falls more vertically than the coarse. As the bed surface rises, the region of predominating fines moves towards the centre and the extent of the coarse-material segregation at the wall increases, but, within the range of normal changes in level, differences in the degree of segregation are unlikely to be large. Should, however, the bed surface be very low, or a bell of extra large dimensions be used for any reason, the falling material will strike the wall at or before reaching the bed surface. In the former case a small rise in the height of the bed will result in a considerable increase in the quantity of coarse material at the

wall, though in the latter case the effect of any change in the surface level would be negligible. Compare Figs. 5 and 6.

(d) *Complications due to Grate Conditions.*

It would be very difficult to imitate, under cold conditions, all the factors obtaining in the grate region in a working producer; in practice, not only are the conditions in the bed constantly changing as the result of combustion, clinkering, porosity of the underlying ash, the type of grate, and the particular manner in which the producer is raked, but the character of the air flow is governed by the persistence or otherwise of the effects associated with the initial distribution of the solid materials. Although, as will be seen later, an attempt to reproduce combustion phenomena and ash-bed formation has been made during the present investigation, it will be well to consider first of all the effect of a central grate on the lines of flow of the materials.

In Figs. 9 and 10 the flow lines obtained by the discharge of alternately coloured horizontal layers can be seen. It was realized that this simple picture does not represent *all* that is happening in this region, as local combustion effects may mask or accentuate the pattern. It was, therefore, necessary to investigate the effect of these phenomena on distribution.

As the quantity of material withdrawn from the base is increased the contour of the surface at the centre changes, with the eventual formation of a central hillock; this condition results in a gradual diminution in the amount of coarse material at the centre, with a consequent increase in the amount of this size grade in the surrounding annular trough before mentioned (see Figs. 6, 7, 8, and 43(a)). The degree to which this central disturbance affects the distribution depends upon the rate at which the fuel bed is replenished, for, when large additions of fuel are made at a time to compensate for considerable withdrawals at the base, the natural stockline associated with the discharge masks the previously mentioned effects, but if, instead, frequent small charges are added this "grate effect" is accentuated (Fig. 43(b)).

III.—METHODS OF DISTRIBUTION CONTROL.

With standard methods of charging there is always an excess of coarse material at the walls and near the centre. The former condition can easily be eliminated by an alteration in the bell/body ratio but this serves only to accentuate the latter (see Fig. 4(a)). Another method that may be used involves the introduction of a deflector ring of such dimensions that the bell may pass freely through it (see Fig. 44(b)); during the early part of the discharge the ring virtually increases the diameter of the bell and throws the material nearer

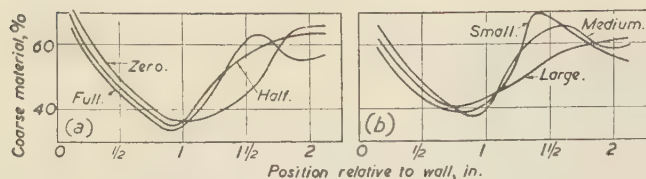


FIG. 43.—Distribution : (a) Influence of discharge upon grate conditions; (b) effect of varying quantity of fuel per charge.

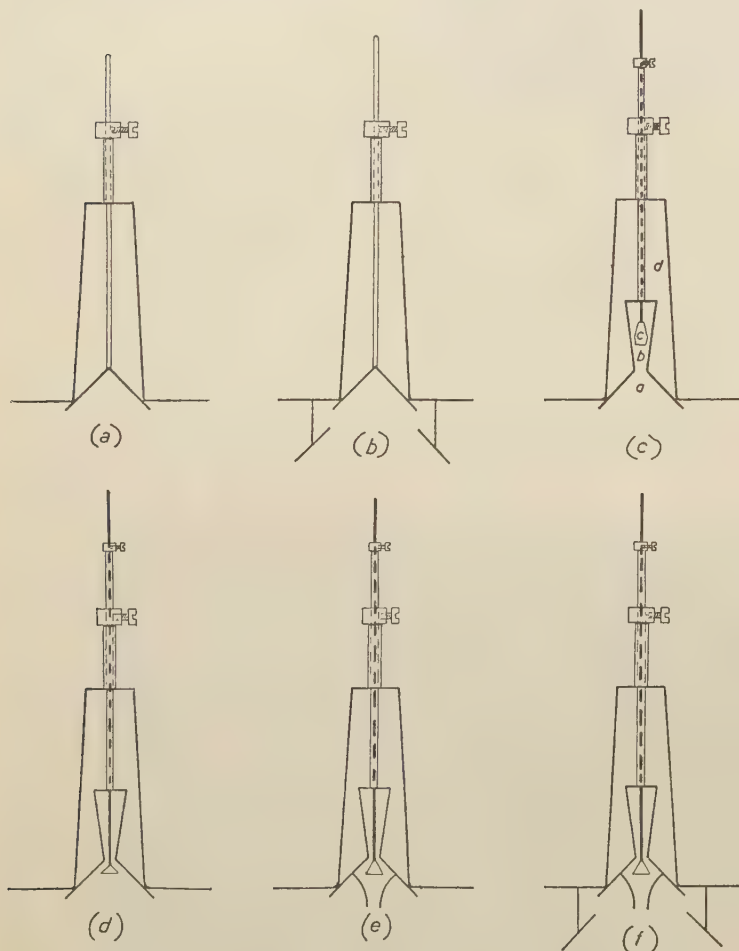


FIG. 44.—Alternative Head-Gear for Experimental Models.

the wall. At a later stage of the bell-drop, when the bell has cleared the ring, the normal type of discharge pattern obtains and the resultant effect is to minimize segregation near the wall. This method of distribution control may be regulated by (i) altering the dimensions of the ring and (ii) changing the relative proportions of material charged over and under the ring. With modification (i) the amount of fines at the wall becomes greater as the extent of the ring increases but the distribution around the centre is unchanged (see Figs. 11, 12, and 45(a)). The simplest way of attaining modification (ii) is to alter the rate of the bell-drop; when this is slow practically all

the charge passes over the ring and gives a pattern similar to that for the increased bell/body ratio. As the rate of opening is increased so the pattern changes and becomes composite in character, each system contributing its individual characteristics (see Fig. 45(b)).

It should be noted, however, that these changes relate to the wall region only; if any change is to be imposed on the central pattern it is necessary to throw some of the material to the centre, and this may be conveniently accomplished by introducing part of the charge vertically through the apex of the bell. Reference to Fig. 44(c) will make this point clear. In this particular modification of the head-gear the top of the bell (*a*, Fig. 44(c)) is cut away and the face extended upwards to form a subsidiary hopper *b* integral with the bell, the orifice being closed by a taper plug *c*; the outer hopper *d* is retained in its normal form. Both hoppers are charged and, when the bell *a* is lowered, the contents of *d* are discharged in the usual manner; on raising the plug *c*, the material in *b* falls vertically into the central depression. It will be appreciated that, by modification of the charging cycle, the bed-surface contour may be altered as desired. In a particular case, when the central region was kept practically level at the end of each cycle, the normal excess of coarse material near the centre was replaced by an excess of fines (see Fig. 13 and curve 1, Fig. 4(b)). Though this design was sufficiently satisfactory to establish the principle of distribution reversal, there would be practical objections to a system involving vertical motion of a plug through the contents of the hopper *b*. To overcome this, the central orifice was closed by means of a diminutive 90° bell, functioning normally (see Fig. 44(d)). In this case,

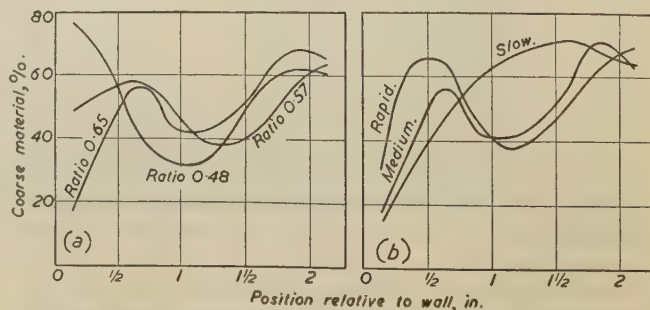


FIG. 45.—Distribution : (a) Influence of deflector-ring dimensions, (b) influence of rate of bell travel through ring (ring/body ratio 0.65).

however, the material no longer falls vertically and the system behaves in effect very similarly to that of a normal, simple bell (see Fig. 14 and curve 2, Fig. 4(b)). In order to retain the bell method of orifice closure and at the same time preserve vertical descent, a curved funnel was fitted to the under surface of the larger bell (see Fig. 44(e)); when this arrangement was used under similar conditions to those already described, the central distribution was reversed (see Fig. 15 and curve 3, Fig. 4(b)) and flexibility of operation was retained.

By a combination of the principles of the deflector ring and the double-bell-and-funnel (Fig. 44(f)), control of distribution over the entire bed was secured. The size of the deflector ring and the operational cycle with the inner bell were chosen to give as uniform a distribution as possible. The ring/throat ratio was 0.57, the rate of bell-drop medium, and sufficient material was charged from the small hopper nearly to fill the central depression at each cycle. By these means, as can be seen by reference to Figs. 41 and 46, the

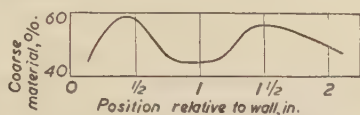


FIG. 46.—Effect of Corrected Distribution with Deflector Ring and Central Charging.

finer and the coarse material were reasonably well distributed, the divergence being within the limits of $\pm 10\%$.

IV.—VISUAL EXAMINATION OF AIR FLOW THROUGH THE BED.

The method employed for visual examination of the air flow was as follows: The selected material, usually marble, was impregnated with potassium iodide, and chlorine introduced into the air blast. For the particular experiments to be described the model was slightly modified, the front and back being of glass, with a grate section cemented in position (see Fig. 47), and all joints rendered gas-tight. This series of experiments may be divided into two groups, the air flow being considered in relation to (1) the charging mechanism and (2) the design of the grate.

It should be observed at the outset that, as all these experiments were carried out in the cold with a bed which remains unchanged in its physical character, similarity with working conditions is not fully realized. It will be appreciated that intumescence followed by compacting will produce a relatively impervious layer over the surface which may considerably alter the gas-distribution characteristics. This may be one of

the reasons for the predominance of "wall fires" which, because of unsatisfactory fuel distribution, may be seriously accentuated. Such effects

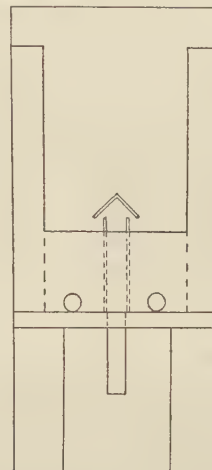


FIG. 47.—Model used for Air-Flow Experiments.

would naturally be minimized with non-caking coals or coke, and these experiments would then more nearly approach operating conditions.

(1) Variations in Charging Methods.

It will be convenient first of all to show two pictures of the blast front as it traverses a uniform burden. The blast is introduced at the centre and, as the velocity is low and resistance uniform, it passes vertically through the material above the grate orifice, with little tendency to spread laterally (see Figs. 16 and 17).

The individual distribution characteristics associated with each of the various types of charging mechanism have already been considered in the present paper; their associated gas flows will now be examined in turn.

With charging from the normal bell (Fig. 44(a)) there is a central region of coarse material through which the blast passes preferentially, the lower resistance accentuating the normal tendency toward central gas flow. Although there is another region of low resistance at the wall, the blast does not extend laterally to a sufficient degree to enter this area (see Figs. 18 and 19). The addition of a deflector ring can exert little influence on this condition, as the ring merely modifies the distribution at the wall region, into which the blast is not penetrating. Thus the blast path (Figs. 20 and 21) accompanying the use of the deflector ring is almost the same as that with the normal bell.

It has already been shown that control of the central region can be secured by introducing material *via* the apex of the bell. When this

orifice is closed by means of a small bell (Fig. 44(d)) the latter again deflects material away from the centre and so the central region of low resistance is still preserved and the effect (see Figs. 22 and 23) is much the same as in the previous cases. The substitution of a rising plug for the bell, such as is shown in Fig. 44(c), allows centrally charged material to fall vertically and thus produces a region of increased resistance over the grate; the blast now passes through an annular region outside the central zone, as may be seen by reference to Figs. 24 and 25. When the plug is replaced by the mechanism shown in Fig. 44(e), the same type of distribution is retained (see Figs. 26 and 27).

(2) Types of Grate.

The air flow from the standard grate (Fig. 47) through a uniform burden has already been described and is illustrated in Figs. 16 and 17. The more usual type of grate employed in gas machines of various designs is, however, some modification of the slotted form shown in Fig. 48. The air

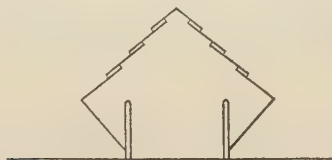


FIG. 48.—Slotted Grate.

flow in this case is shown in Figs. 28 and 29, and it is evident that the spread is more uniform in the neighbourhood of the grate—the dead space over the apex, particularly noticeable in Figs. 16 and 17, now being eliminated, thus demonstrating the superiority of the slotted variation.

V.—QUANTITATIVE MEASUREMENT OF GAS DISTRIBUTION.

In any bed where segregation occurs, the resistance to the air blast will vary according to the texture of the bed; thus if the pressure drop between various points over the base of the burden and atmosphere be measured, it will be found that the maximum blast obtains where the pressure difference is least. To study this aspect of the problem, the original slice model was modified. A new back plate of thin plywood was fitted, the lower region being covered on the outside with $\frac{1}{16}$ -in. sheet rubber. A number of small hypodermic needles, together with their clearing wires, were inserted through the backing until the points—slanting faces downwards—extended midway between the walls. The clearing wires were withdrawn and the butts connected by means of rubber tubing to a series of inclined

manometers. The grate was of the simplest type, being a section of an open pipe fitted with a plain conical hood (see Fig. 47). This grate, together with the front and back plates, was cemented in position before the commencement of the experiment, so rendering the model gas-tight. The model was charged in the requisite manner and the air intake was connected to a blower *via* an orifice meter, to measure the flow. A photograph of the general arrangement of the apparatus is shown in Fig. 42.

Most of the gas-distribution experiments were carried out with the needles arranged at equal intervals along a horizontal plane immediately over the apex of the hood. In a preliminary experiment the model was filled to the normal bed-surface height of 2 in. above the hearth ($3\frac{1}{2}$ in. below the top plate) with a uniform 20/40 mesh burden, hand-charged and levelled. The needles were then inserted and the air flow was set at 0.4 cu.ft./min. It will be seen from Fig. 49, where

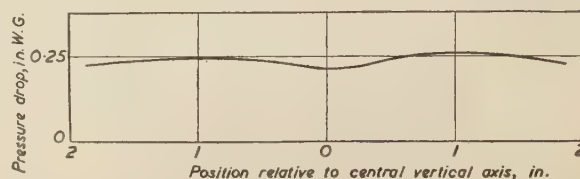


FIG. 49.—Pressure Differences Across Uniform Bed.

the pressure differences are plotted against position in the bed, that, although the variation of the pressure differences is very small, it shows a regular pattern, with slight falls at centre and wall. This flow of 0.4 cu.ft./min. is at least double that used in subsequent experiments, so that pressure changes other than those caused by segregation in the burden may be considered as negligible.

The general experiments in this section may be considered in relation to (1) variation of bed-surface contour and (2) variation of grading limits and quality. Under (1) two main types of contour may occur, as in blast-furnace work, *viz.*, the V and the M. With the former, fines predominate near the wall and with the latter between the wall and the centre (see Figs. 5 and 6). Charging may also be controlled to give a horizontal bed surface.

In this group of experiments the burden consisted of 10/20 and 40/60 mesh mixtures.

(1) Variation of Bed Surface.

(a) V Contour.

To produce the V contour a large bell (bell/body ratio, 0.42) was employed and the material was charged into the empty model until the normal bed height was reached; the average fall to the

bed was thus sufficient to ensure the correct contour and its associated distribution. The air cock, supplying 0.2 cu.ft./min., was opened and pressures were measured; these pressures are plotted in Fig. 50(a). It will be seen that the position of

is substantially the same whether the burden had descended or remained stationary.

(c) *Surfaces Obtained by Compensated Charging.*

In each of the cases just described the charging was carried out from a simple bell, the only variation to the head-gear being in respect of the bell diameter. It has already been shown that by using compound charging mechanisms more control can be exercised over the degree of segregation taking place; the effects of such controlled distribution on the pressure drop across the bed were investigated.

The head-gear illustrated in Fig. 44(f) and the charging cycle were arranged to give an approximately horizontal bed surface. Charging was continued until the normal height of the bed was attained, the pressure differences being recorded as before. The corresponding curves are shown in Fig. 50(c); curve 1 shows that under these conditions there is now no marked pressure-drop minimum at any point in the bed. When such an experiment was repeated under normal operational conditions of charge and discharge, employing the same head-gear and charging cycle, a pressure-drop minimum appeared at the wall, as in curve 2. Although this particular charging modification gives a measure of compensation, the quantity of fines at the wall is still insufficient and any motion of the bed produces filtration of fine material, so creating channels in which the resistance to the air flow is relatively less. When the head-gear was changed to that illustrated in Fig. 44(d) in combination with the deflector ring shown in Fig. 44(b), the predominance of coarse material at the centre of the bed—which condition is associated with this type of charging—resulted in a pressure-drop minimum occurring in this region in addition to that occurring at the wall (see curve 3, Fig. 50(c)).

Further experiments, in which the charging was controlled to give adequate fines at the walls while still preserving overall uniform distribution, were carried out with charge and discharge of burden and under these conditions much more uniform pressure-drop curves were obtained, as can be seen in Fig. 50(d). It should be noted that these latter experiments were carried out in a model with a narrower body.

(2) *Influence of Grading upon the Pressure Drop.*

(a) *Grading Limits.*—The larger grading limit for the materials was kept at 10 mesh, while the lower was varied from 60 to 100 mesh; in general, a uniform quality was preserved (i.e., equal-volume mixtures of 10/20, 20/40, 40/60 mesh, and 10/20, 30/60, 60/100 mesh, respectively). These mixtures were charged to give the requisite contour, and the pressure differences were recorded

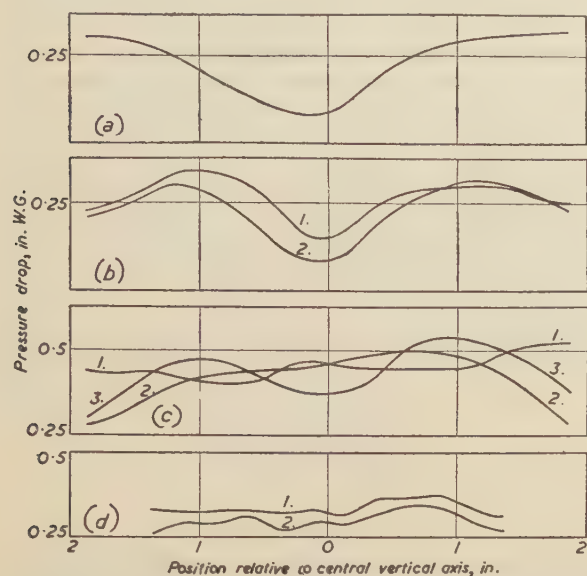


FIG. 50.—Pressure Differences Across Mixed Burden: (a) V bed-surface; (b) M bed-surface; (c) and (d) compensated charging.

minimum pressure drop is at the centre, corresponding with the position of maximum coarse material.

(b) *M Contour.*

The M contour was obtained by charging the material from a normal-sized bell (bell/body ratio, 0.32). In this case the empty model was filled to the normal level as in the previous experiment, but discharges were made from two apertures (normally closed) at the base, corresponding additions being made to keep the surface height constant until the material first charged had descended to the bottom of the grate. The air cock was then opened and the pressures were measured; these pressures are shown in curve 1, Fig. 50(b) and it will be seen that whilst the central low pressure drop persists, another region of low pressure drop has appeared at the wall.

In order to show that the pressure effects at the wall are not solely a result of the vertical movement of the burden, a similar experiment was carried out in which the M contour was initially formed and was maintained throughout the charging process. When the normal bed-surface height was reached, the air was turned on and the pressure drops measured as before; these are plotted in curve 2, Fig. 50(b) and it can be seen that the variation of pressure drop across the bed

as before. It can be seen from Fig. 51, (a) and (b), (for V and M contours respectively) that as the

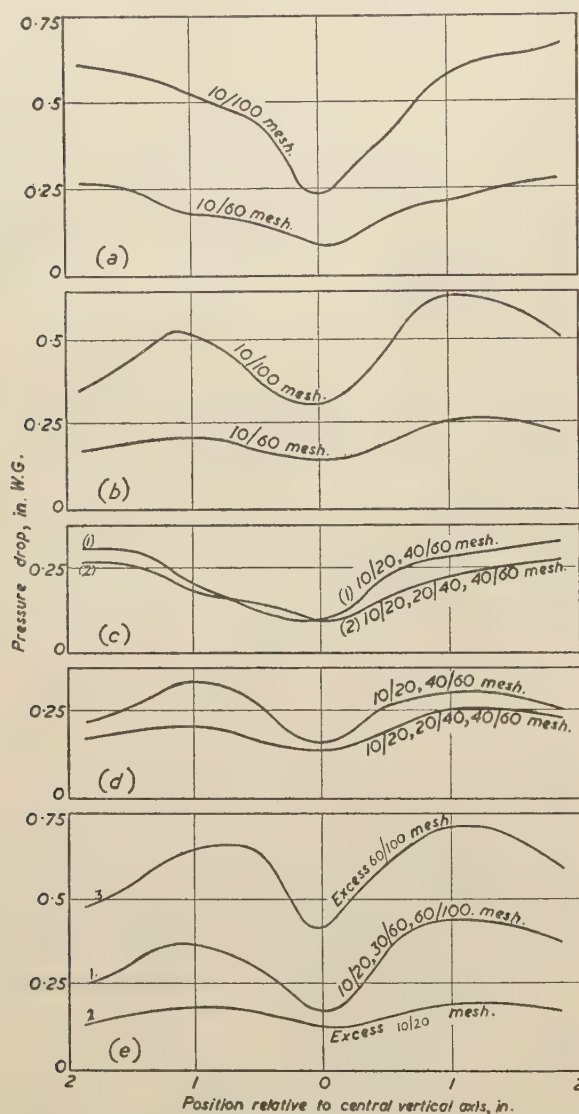


FIG. 51.—Pressure Differences Across Mixed Burden with Variations in Grading Limits: (a) and (c) V bed-surface; (b), (d), and (e) M bed-surface.

grading limits are extended the pressure differences increase and the minima become more markedly accentuated.

(b) *Grading Quality*.—The quality of a grading between specified limits depends upon the relative quantities of the components; differences will be observed in the behaviours of uniform and irregular mixtures. In the former case the pressure differences are relatively smaller and the variations less. Two examples will serve as illustrations of this.

For burdens of (1) equal quantities of 10/20, 20/40, and 40/60 mesh material and (2) equal

quantities of 10/20 and 40/60 mesh material, charged to give V and M bed-surfaces in both cases, the recorded pressure differences are shown in Fig. 51, (c) and (d), respectively.

In mixtures where some particular range within the grading predominates, the characteristic pressure-difference curve associated with any bed-surface contour is modified according to the degree of predominance of coarse or fine material; for example, the greater the quantity of coarse particles the smaller are the pressure differences and variations observed, whilst when fines predominate the pressure differences are greater and the variation is accentuated. Examples of the operation of this factor are provided by curves 1, 2, and 3 (Fig. 51(e)), for which the respective conditions were:

- Curve 1: Equal quantities of 10/20, 30/60, and 60/100 mesh. (Control mixture.)
- Curve 2: Double excess of 10/20 mesh, with equal quantities of 30/60 and 60/100.
- Curve 3: Double excess of 60/100 mesh, with equal quantities of 30/60 and 10/20.

VI.—THE ASH-BED.

Experimental Investigation of Ash-Bed Formation.

In actual gas-producer practice, the condition of the ash-bed certainly plays an important rôle in modifying the particular air distribution determined by the segregation characteristics, and an attempt was made to approach such conditions in the laboratory studies. A similar model to that employed in the visual air-flow experiments was used, but the materials were changed to 10/40 mesh lump ammonium carbonate mixed with varying percentages of 10/40 mesh coke; the air blast was dried and preheated to 80–100° C. During the experiments the ammonium carbonate was thus decomposed at a convenient rate (simulating the combustion of fuel) and the coke, which by reason of its similar density and size was uniformly distributed throughout the bed, remained behind as the “ash.” The similarity may not be complete as, under the experimental conditions, the “ash” was not clinkered; on the other hand, gas viscosities were nearer those obtaining in the working machine. Nevertheless, it still remains to be ascertained to what extent these pictures would be modified by clinkering of the ash.

A sketch of the experimental apparatus is shown in Fig. 52. Air is delivered from a small rotary blower *via* a drying tower and flow-meter to the copper heating-coil situated as close as possible to the model. The materials were first of all hand-charged to give a level bed surface of normal depth. The air flows were of the order of 0.3 cu.ft./min., but care was taken to avoid teetering. The draught was continued until a volume of carbonate equivalent to one hopperful had been

volatilized, when a normal head-gear (Fig. 44(a)) was fitted and the bed replenished by the requisite addition. This process was repeated until two further charges had been introduced. Photographs of the bed were taken at the commencement of the experiment, and subsequently before and after each addition of material from the bell. The progress of the changes may be best illustrated by consideration of the case with the greatest "ash" content (25%) first, the respective photographs for which are reproduced in Figs. 30 to 36. It should be noted that the "ash" (potential or otherwise) appears as dark specks merging into dark areas as the carbonate is volatilized, so representing the ash-bed in formation. Keeping in mind the fact that there is no change in the ash-bed while charging is in progress, *i.e.*, Figs. 31 and 32, 33 and 34, 35 and 36 represent unchanged ash-bed conditions, it will be seen that the ash gradually extends and eventually covers a dome-

improved apparatus constructed from materials at hand. The body consisted of the refractory lining of a small gas furnace of 3½-in. dia., fitted at the base with an air intake and simple grate as shown in Fig. 47. No top plate or gas offtakes were fitted and all the charging was done by hand. No means was provided for raking out, and the individual experiments were therefore not of long duration.

The well was first covered with a layer of 10/20 mesh firebrick up to the level of the apex of the grate, overcharged with a thin layer of 4/10 mesh coal, which was ignited by means of a suitable gas/air mixture introduced through the intake. As soon as the coal layer was burning freely at a uniform red heat, the selected burden was charged to a depth of 2½ in., and the air flow maintained at the required value. The time taken between charging and the initial penetration of the bed surface by the flame, and the general character of the bed were noted. When it was desired to arrest combustion the air was replaced by nitrogen and, after cooling sufficiently, the contents were examined in greater detail. In general it was observed that large material ignited and burnt more readily than small. This effect may be partly attributed to the greater pressure drop in the latter case, and possibly earlier teetering, leading to channelling. Other factors may also be involved, and the problem requires further investigation. In all cases the formation of a coking zone around the grate restricts the vertical air flow and combustion is extended to the wall, at which region the flame first breaks through the bed; the greater the quantity of coarse material near the wall the sooner does this phenomenon take place. This was indicated by further experiments in which segregation was ensured by inserting concentric cylinders vertically on the bed and adding the different sizes of fuel through the cylinders. In the first case (a) 40/60 mesh coal was charged at the centre; this was surrounded by similar coal but of 4/10 mesh; in the second case (b) these conditions were reversed. In case (b) the flame took about four times as long to break through the bed, mainly as the result of channelling, and the overall degree of combustion was very much greater. When the coarse material was located between the centre and wall, the results were intermediate.

Difficulties due to teetering of the fine-mesh fuel could be overcome to some extent by wetting the coal; for example, in one experiment where some 20% of water was incorporated with under 60 mesh coal, combustion was more complete and coalescence of the particles much less in evidence.

Combustion rates for a given air flow were in general greater as the size of the fuel increased, within reasonable limits, and with mixtures the

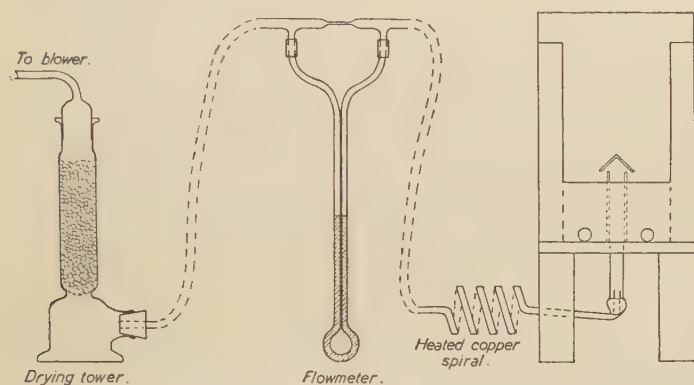


FIG. 52.—Apparatus for Artificial Ash-Bed Studies.

shaped region around the hood, which region would ultimately extend to the wall; owing to the absence of clinkering there is little change in the resistance to air flow. If, however, one presupposes clinkering, with consequent increased resistance to the draught, it can be seen that the lateral spread of the ash-bed may be considerably accelerated, so deflecting the main air flow outwards. With reduced ash contents the results are similar, but the ash-bed is less extensive. Figs. 37 and 38, and 39 and 40 relate to ash contents of 15% and 5% respectively and are the initial and final stages as described above.

VII.—COMBUSTION EXPERIMENTS IN A SMALL-SCALE MODEL.

At this stage of the investigation it was decided to attempt the operation of a ¼th scale working model of a static producer, to run in conjunction with the various distribution and air-flow experiments already described; while this was under construction, preliminary trials were made in an

results were intermediate, *i.e.*, lower than those relating to the smaller-size component but not so great as those associated with the larger coal.

VIII.—CONCLUSIONS.

(1) Whilst changes in the bell-drop, the bell/body ratio, and the bed-surface level may alter the size distribution of fuel in a producer, it is not possible to secure a uniform distribution without additional means of control.

(2) Alternative methods of charging have been suggested whereby a uniform or any desired segregation of the solid materials can be attained.

(3) The predominant gas flow has been shown (visually and by measurement) to follow the region of maximum coarse material in the fuel bed.

(4) A more uniform grading of the fuel gives a reduced tendency to channelling, while an increase in the amount of fines produces the opposite effect.

(5) The ash-bed forms around the central grate and extends outwards towards the wall; this results in an outward deflection of the draught.

(6) Caking of the fuel in the early stages of combustion induces an outward movement of the draught.

ACKNOWLEDGMENTS.

The experimental work embodied in this paper was carried out at the Imperial College of Science and Technology, South Kensington, for the British Iron and Steel Research Association, by whom it was also financed.

THE PHYSICAL PROPERTIES OF A SERIES OF STEELS.—PART II.*

A REPORT FROM THE PHYSICS DIVISION, THE NATIONAL PHYSICAL LABORATORY (TEDDINGTON).

(Under the direction of Dr. E. Griffiths, F.R.S.)

Paper No. 23/1946 of the Alloy Steels Research Committee (submitted by the Thermal Treatment Sub-Committee).

(Fig. 28 = Plate IX.)

SYNOPSIS.

The subject of the paper is a series of twenty-two steels, comprising eight carbon, eight alloy, and six high-alloy steels. The present account concerns work carried out on these steels subsequent to the publication of the first report.

Specific-heat measurements have been extended so that data are available up to about 1300° C. on all steels, a new method being developed for measurements above 900° C. Determinations of the coefficients of expansion of fourteen steels have been made, completing the series of steels up to about 1000° C., but excluding the steel of eutectoid composition. Electrical-resistivity measurements have been extended on all steels up to 1300° C. and measurements have been made of thermal conductivity of a 0.8% carbon steel (steel 7), up to 1000° C. and of a 13% manganese steel (steel 13) up to 850° C.

In addition, the report includes the results of a detailed examination of the effect of heat-treatment on the electrical resistivity and thermal conductivity of the 13% manganese steel and a note on the estimation of the thermal conductivity of steels from electrical-resistivity data.

Introduction.

THE investigation relates to further determinations of certain physical properties of a number of steels

TABLE I.—Analyses of the Steels Examined.

Steel	C, %	Si, %	Mn, %	S, %	P, %	Cr, %	Ni, %	W, %	Mo, %	V, %	Cu, %	Al, %	As, %	Heat-Treatment.	Density at 15° C.
<i>Carbon Steels.</i>															
1	0.06	0.01	0.38	0.035	0.017	0.022	0.055	Nil	0.030	Nil	0.08	0.001	0.039	Annealed at 930° C.	7.871
2	0.08	0.08	0.31	0.050	0.029	0.045	0.07	Nil	0.020	Nil	Trace	0.002	0.032	Annealed at 930° C.	7.856
3	0.23	0.11	0.635	0.034	0.034	Trace	0.074	Nil	Nil	Nil	0.13	0.010	0.036	Annealed at 930° C.	7.859
5	0.415	0.11	0.643	0.029	0.031	Trace	0.063	Nil	Nil	Nil	0.12	0.006	0.033	Annealed at 860° C.	7.854
6	0.435	0.20	0.69	0.038	0.037	0.03	0.04	Nil	0.01	Nil	0.060	0.006	0.024	Annealed at 860° C.	7.844
7	0.80	0.13	0.32	0.009	0.008	0.11	0.13	Nil	<0.01	Nil	0.070	0.004	0.021	Annealed at 800° C.	7.851
101	0.84	0.13	0.24	0.014	0.014	Trace	Trace	Nil	Nil	Nil	0.02	0.004	0.009
8	1.22	0.16	0.35	0.015	0.009	0.11	0.13	Nil	0.01	Nil	0.077	0.006	0.025	Annealed at 800° C.	7.830
<i>Alloy Steels.</i>															
4	0.23	0.12	1.51	0.038	0.037	0.06	0.04	Nil	0.025	Nil	0.105	0.015	0.033	Annealed at 860° C.	7.849
9	0.325	0.18	0.55	0.034	0.032	0.17	3.47	Nil	0.04	0.01	0.086	0.006	0.023	Annealed at 860° C.	7.855
10	0.33	0.17	0.53	0.033	0.031	0.80	3.38	Nil	0.07	0.01	0.053	0.006	0.028	Annealed at 860° C., then re-	7.847
11	0.325	0.25	0.55	0.025	0.018	0.71	3.41	Nil	0.06	0.01	0.120	0.008	0.023	heated to 640° C. and cooled	7.848
12	0.34	0.27	0.55	0.003	0.024	0.78	3.53	Nil	0.39	Nil	0.050	0.007	0.037	in furnace.	7.859
19	0.315	0.20	0.69	0.036	0.039	1.09	0.073	Nil	0.012	Nil	0.066	0.005	0.028	Annealed at 860° C.	7.842
20	0.35	0.21	0.59	0.031	0.028	0.88	0.26	Nil	0.20	Trace	0.12	0.004	0.039	Annealed at 860° C., then re-	7.845
														heated to 640° C. and cooled	
														in furnace.	
21	0.485	1.98	0.90	0.047	0.044	0.04	0.156	Nil	Nil	Nil	0.637	0.007	0.029	Annealed at 930° C.	7.725
<i>High-Alloy Steels.</i>															
13	1.22	0.22	13.00	0.010	0.038	0.03	0.07	Nil	Nil	Nil	0.070	0.004	0.038	Heated to 1050° C. and cooled	7.870
														in air.	
14	0.28	0.15	0.89	0.003	0.009	Trace	28.37	Nil	Nil	Nil	0.030	0.012	0.027	Heated to 950° C. and cooled	8.161
														in water.	
15	0.08	0.68	0.37	0.011	0.022	19.11	8.14	0.60	Nil	Nil	0.030	0.004	0.025	Heated to 1100° C. and cooled	7.916
														in water.	
16	0.13	0.17	0.25	0.024	0.018	12.95	0.14	Nil	Nil	0.012	0.060	0.034	0.015	} Heated at 960° C. in air, T. 2 hr. at 750° C. and air-cooled.	7.745
17	0.27	0.18	0.28	0.022	0.022	13.69	0.20	0.25	0.01	0.022	0.074	0.031	0.003		7.741
18	0.715	0.30	0.25	0.028	0.018	4.26	0.067	18.45	Trace	1.075	0.064	0.004	0.035		8.691

* Received August 25, 1945. This paper is published by the Alloy Steels Research Committee. The views expressed in it are the authors' own and are not necessarily endorsed by the Committee as a body.

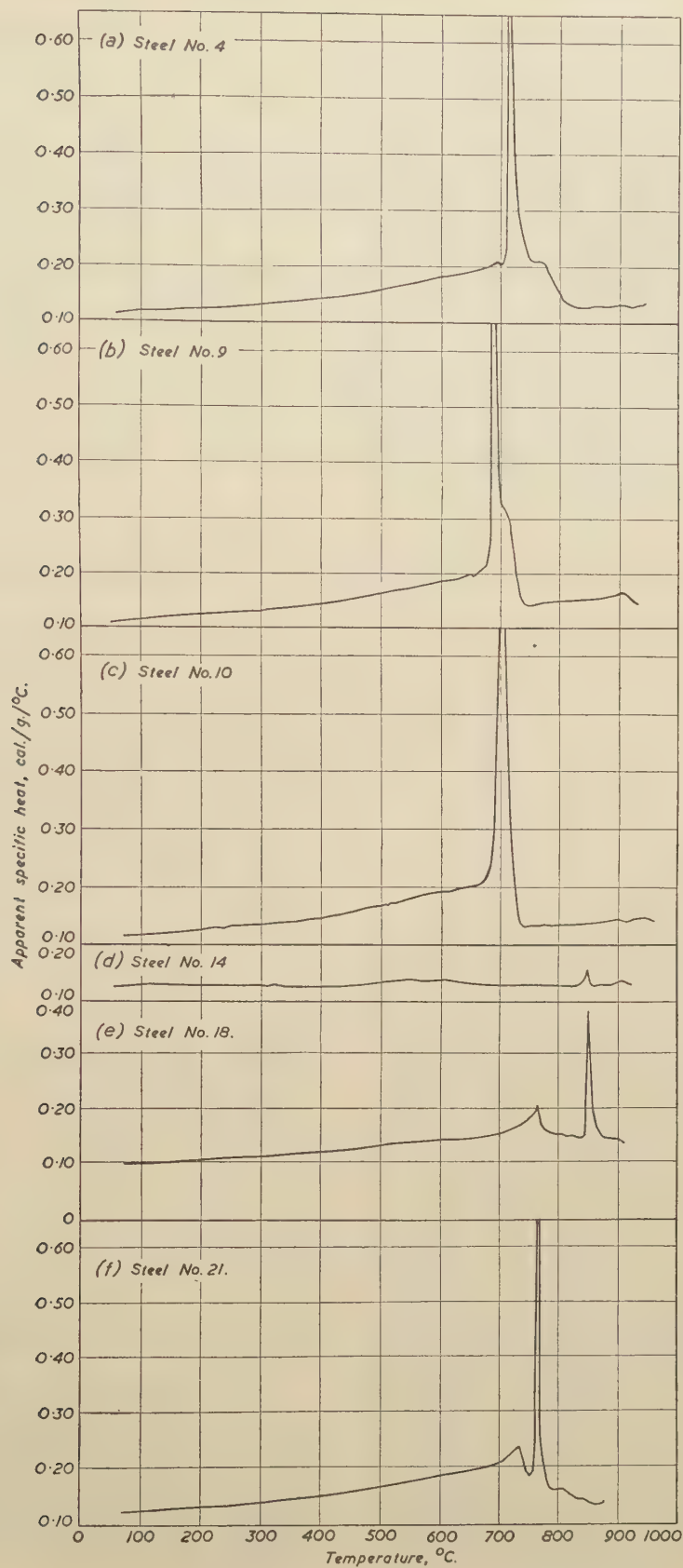


FIG. 1.—Mean Apparent Specific-Heat Curves for Various Steels.

TABLE IV.—*Mean Apparent Specific Heats of Alloy Steels over 50° C. Ranges (Expressed as cal./g./° C.).*

Temp. Range, ° C.	Steel.														Pure Iron.
	4.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.	
50-100	0.114	0.115	0.118	0.117	0.116	0.124	0.119	0.122	0.113	0.113	0.098	0.118	0.114	0.119	0.112
100-150	0.118	0.120	0.121	0.123	0.121	0.129	0.120	0.126	0.119	0.117	0.102	0.122	0.119	0.122	0.117
150-200	0.122	0.125	0.125	0.125	0.125	0.133	0.120	0.127	0.123	0.122	0.104	0.125	0.123	0.125	0.122
200-250	0.126	0.128	0.128	0.129	0.128	0.136	0.119	0.129	0.127	0.127	0.108	0.128	0.126	0.129	0.126
250-300	0.130	0.131	0.134	0.131	0.133	0.139	0.119	0.131	0.132	0.131	0.111	0.132	0.130	0.133	0.130
300-350	0.135	0.136	0.139	0.136	0.139	0.141	0.118	0.134	0.138	0.136	0.116	0.137	0.136	0.138	0.135
350-400	0.141	0.141	0.143	0.142	0.145	0.143	0.117	0.136	0.145	0.143	0.120	0.142	0.142	0.144	0.140
400-450	0.147	0.148	0.151	0.149	0.152	0.142	0.119	0.139	0.151	0.151	0.125	0.149	0.145	0.151	0.146
450-500	0.155	0.158	0.161	0.159	0.160	0.138	0.124	0.142	0.163	0.162	0.132	0.157	0.167	0.159	0.155
500-550	0.166	0.168	0.172	0.170	0.172	...	0.129	0.150	0.174	0.173	0.139	0.166	0.166	0.168	0.165
550-600	0.177	0.179	0.185	0.182	0.184	...	0.130	0.155	0.186	0.186	0.143	0.177	0.176	0.179	0.175
600-650	0.186	0.189	0.194	0.192	0.197	...	0.125	0.151	0.195	0.201	0.147	0.185	0.184	0.187	0.185
650-700	0.200	0.201	0.212	0.212	0.251	...	0.123	0.149	0.209	0.221	0.162	0.200	0.197	0.198	0.198
700-750	0.246	0.248	0.281	0.230	0.297	...	0.124	0.150	0.216	0.237	0.171	0.258	0.236	0.216	0.232
750-800	0.196	0.144	0.133	0.136	0.152	...	0.123	0.153	0.165	0.187	0.171	0.223	0.211	0.226	0.218
800-850	0.133	0.149	0.136	0.136	0.150	...	0.127	0.155	0.193	0.230	0.163	0.135	0.136	0.146	0.180
850-900	0.128	0.153	0.139	0.137	0.152	...	0.126	0.153	0.160	0.157	0.176	0.137	0.170
900-950	0.143	0.138	0.154	0.226

TABLE V.—*Mean Apparent Specific Heats of Alloy Steels over Ranges of less than 50° C. (Expressed as cal./g./° C.).*

Temp. Range, ° C.	Steel.													Pure Iron.
	4.	9.	10.	11.	12.	14.	15.	16.	17.	18.	19.	20.	21.	
600-640	...	0.18
640-650	...	0.19 ₅
650-660	0.19 ₅	0.19 ₅	0.20	0.20	0.21
660-670	0.19 ₅	0.20 ₄	0.21	0.20	0.21
670-680	0.19 ₅	0.22 ₄	0.22	0.22	0.22
680-690	0.20 ₄	0.80	0.29	0.26	0.25
690-700	0.20 ₅	0.53	0.64	0.49	0.37
700-710	0.22 ₁	0.32	0.64	0.69	0.64	0.22 ₅	0.24 ₅	...	0.22	0.21	0.21	0.21
710-720	0.64	0.29 ₅	0.32	0.42	0.53	0.24 ₁	0.25 ₅	...	0.23	0.22	0.22	0.22
720-730	0.38	0.22 ₁	0.18	0.25	0.46	0.22 ₇	0.26 ₅	...	0.24	0.23	0.23	0.23
730-740	0.27	0.16 ₁	0.13	0.16	0.26	0.19 ₄	0.22 ₇	...	0.31	0.49	0.22	0.24
740-750	0.22 ₅	0.14 ₅	0.13	0.14	0.18	0.18 ₄	0.20 ₅	...	0.80	0.77	0.19	0.25
750-760	0.21 ₅	0.19 ₅	0.19 ₅	0.35	0.32	0.19	0.27
760-770	0.21 ₅	0.18 ₅	0.18 ₄	0.24	0.23	0.92	0.22
770-780	0.20 ₄	0.18 ₅	0.16 ₄	...	0.19	0.20	0.21
780-790	0.18 ₅	0.18 ₅	0.15 ₅	...	0.16 ₅	0.16	0.20
790-800	0.16 ₅	0.18 ₄	0.15 ₄	...	0.15 ₅	0.15 ₅	0.19
800-810	0.12 ₅	...	0.15 ₅	0.25 ₅
810-820	0.12 ₅	...	0.15 ₅	0.33 ₅	...	0.20	...	0.20	...
820-830	0.12 ₅	...	0.21 ₇	0.20 ₅	...	0.18	...	0.16	...
830-840	0.12 ₅	...	0.23 ₄	0.18 ₅	...	0.15	...	0.15 ₅	...
840-850	0.14 ₅	...	0.19 ₅	0.16 ₅	0.13	...
850-860	0.12 ₇	0.26 ₂	...	0.13 ₁
860-870	0.17 ₄	...	0.12 ₈
870-880	0.15 ₅	...	0.12 ₈
880-890	0.14 ₅
890-900	0.14 ₅	0.17
900-910	0.14 ₅	0.54
900-930	0.13 ₅	0.15 ₅	0.14 ₅	0.14	0.28
900-940	...	0.15 ₅	0.25

the temperature of the specimen remained constant at the transformation point. This was the only one of the alloy and high-alloy steels which showed a definite halt with the absorption of a latent heat.

For specific-heat data on the carbon steels over the same temperature range, reference should be made to the previous work on this subject.¹ For purposes of comparison, data for iron of purity greater than 99.9% are included in Tables III.,

IV., and V. Further details on the thermal capacity of iron have been published elsewhere.²

DISCUSSION OF RESULTS.

(a) *Temperatures of Heat Absorption.*

The temperatures at which the specific heats rise to maxima are given in Table VI. A distinct similarity is to be noted between the systems of peaks of steels 14 and 15 (in which the

TABLE VI.—*Peaks in Specific-Heat Curves.*

Steel.	Temperature of Peaks, ° C.				
4	695 †	714 *	760	870	910
9	555	648	686 *	708	910 †
10	590	705 *	910	935 †	
11	590	702 *	895	935 †	
12	660	670	705 *	910	940
13	390				
14	305	530	845 †	910	
15	350	570 †	860	902	
16	650 †	720 *	830 *		
17	650	728 *	810 *		
18	550	760 †	850 *		
19	745 *	900			
20	682	742 *			
21	730 †	764 *	810	845	

* Indicates a major peak.

† Indicates a small peak.

The remainder are minor peaks.

iron is in the gamma state). Similarly, steels 16 and 17 both show two prominent peaks and one smaller peak.

(b) Application of Grüneisen's Law.

Grüneisen's investigations into the theory of the solid state suggest that for any one substance α/C is approximately constant (independent of temperature), where α is the coefficient of expansion and C the specific heat. The law has been tested over wide ranges of temperature for various non-ferrous metals, such as silver and aluminium, and might be expected to hold for α -iron with one value of the constant, and for γ -iron with a different value. To show how far the law is obeyed by

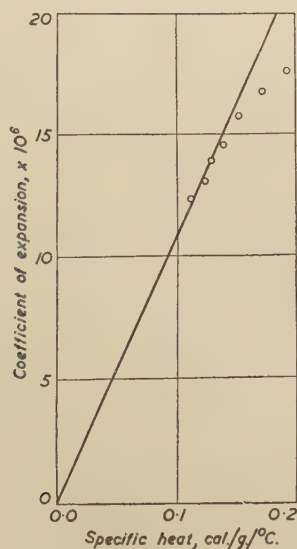


FIG. 2.—Grüneisen's Law for Steel 3.

steels, Fig. 2 shows the specific heat of steel 3 (a simple carbon steel) against its expansion coefficient ($1/l)(dl/dt)$ at temperatures of 50°, 150°, &c., to 650° C. It will be seen that the first three points lie satisfactorily on a line through the origin, thus conforming to Grüneisen's law, but above 250° C. the points deviate regularly from the law. This deviation could be due either to a falling-off in the coefficient of expansion, or to an anomalous increase in the specific heat. The latter cause might be anticipated if part of the observed specific heat is really due to the gradual incidence of some heat absorption which only attains its maximum value when the peak observed at 720° C. is reached. If this assumption is made it becomes possible to separate the true specific heat from the contributions due to these absorptions of heat by calculating the true specific heat from the observed coefficient of expansion and by use of the factor appropriate to the straight line in Fig. 2. The result of this calculation is shown

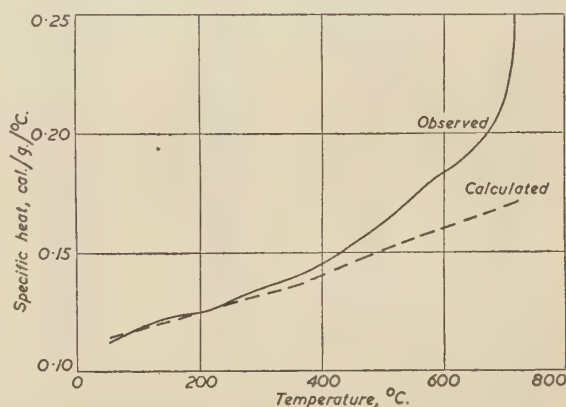


FIG. 3.—Specific Heat of Steel 3.

in Fig. 3, from which Table VII., giving total heats, has been compiled.

TABLE VII.—*Total Heat of Steel 3 from 50° C. to t° C.*

t° C.	Total Heat, cal./g.		
	From Grüneisen's Law.	By Experiment.	Excess.
50	0	0	0
100	5.8	5.8	0.0
150	11.8	11.8	0.0
200	17.9	18.0	0.1
250	24.3	24.4	0.1
300	30.8	31.0	0.2
350	37.5	37.9	0.4
400	44.4	45.0	0.6
450	51.6	52.5	0.9
500	59.0	60.4	1.4
550	66.7	68.8	2.1
600	74.6	77.7	3.1
650	82.6	87.1	4.5
700	91.0	97.2	6.2

The last column shows the excess heat absorption up to any temperature t° C., and it can be seen

that it reaches 4.5 cal./g. at 650° C.—well below the temperature of the peak.

Similar calculations were carried out for steel 16. Here the observations of coefficient of expansion and of specific heat in the γ -form (above the transformation temperature) permitted Grüneisen's law to be verified for the material in the γ -state, so that the data given in Table VIII. extend right through the peak.

TABLE VIII.—Total Heat of Steel 16 from 50° C. to t° C.

t° C.	Total Heat, cal./g.		
	From Grüneisen's Law.	By Experiment.	Excess.
50	0	0	0
100	5.6	5.7	0.1
150	11.5	11.6	0.1
200	17.7	17.7	0.0
250	24.0	24.1	0.1
300	30.6	30.7	0.1
350	37.25	37.6	0.35
400	43.9	44.8	0.9
450	50.7	52.4	1.7
500	57.9	60.5	2.6
550	65.2	69.2	4.0
600	72.4	78.5	6.1
650	79.7	88.3	8.6
700	86.9	98.7	11.8
750	94.2	109.5	15.3
800	101.4	117.7 ₅	16.3 ₅
850	108.7	127.4	18.7
900	116.1	135.4	19.3
950	123.5	(143.0)	(19.5)

In this case it will be noted that the excess heat rises at the higher temperatures to an approximately constant value of 20 cal./g., which includes the heat absorbed within the transformation peak.

Grüneisen's law may be utilized in another way. Each steel gives in general two values for the Grüneisen ratio α/C , one for the α -form, and one for the γ -form. If these ratios are plotted against the atomic percentage of other elements than iron in the steel, as in Fig. 4, it will be seen that an approximate value for the ratio can be estimated from composition alone, and hence the specific heat of a steel, either in the α - or the γ -state, can be assessed from a knowledge of its expansion coefficient at temperatures sufficiently far from any transformations. It should be noted, however, that steel 18, with 17.5% of additional elements, gives a Grüneisen ratio of 116, which is much higher than the value appropriate to an α -iron of this composition (93) but much lower than the value for γ -iron (150). The other anomalous point is for steel 8 in the γ -state at 850° C., for which the ratio is 218 instead of 150. This steel had an exceptionally high coefficient of expansion immediately above the transformation point, and might have shown a more normal ratio if observa-

tions to higher temperatures had been available. This supposition is confirmed from specific-heat

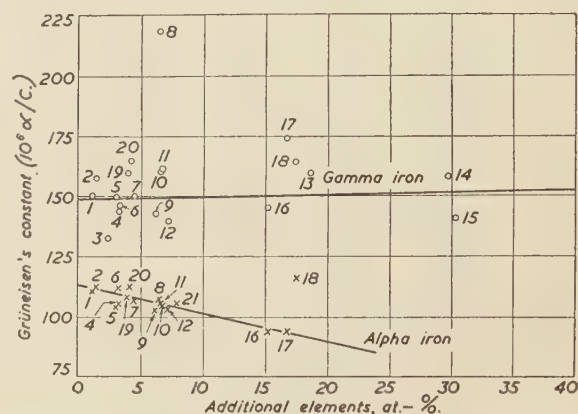


FIG. 4.—Grüneisen's Ratio for 21 Steels.

data given in Section IB., e.g., at 950° C. the value of the constant is 152×10^{-6} .

(c) Specific Heat and Composition.

The specific heats of solid solutions, and even of chemical compounds such as the alkali halides, frequently differ only slightly from the values calculated by adding together the contributions due to the constituents in the free state. Such a relation would not be expected to hold for steels at temperatures where processes involving the absorption of heat are operative, but it is of interest to examine whether the specific heat is additive at lower temperatures. In these calculations it is convenient to work in terms of atomic composition, since the atomic heat (the product of the specific heat and atomic weight) is nearly constant for all the elements concerned except carbon and, to a less extent, silicon. This explains why a given quantity by weight of an element of high atomic weight, such as tungsten, in a steel lowers its specific heat. Table IX. shows the atomic heat in calories per gramme-atom per degree centigrade for the elements reported in the analyses of the 22 steels which have been studied. These atomic heats have been taken from International Critical Tables, vols. 1 and 5, except that the thermal unit has been changed from the joule to the calorie. The values for carbon are much lower, and are given in Table X.

The specific heats of some of these elements are not known with precision above about 50° C., at which temperature the results now reported for steels commence. Fortunately, however, the contributions from these particular elements are quite small, and the values in Table XI. have been assumed to apply to 100° C.—a temperature high enough for the results to be free from the slight uncertainties which occur at the start of an

TABLE IX.—*Atomic Heats of Elements.*

Element.	Temperature, ° C.	Atomic Heat, cal./g. atom/° C.
Aluminium	20	5.78
	150	6.22
Arsenic	50	6.17
	50	6.46
Chromium	0	5.36
	20	5.5
	50	5.64
	200	6.12
Copper	0	5.82
	100	5.98
	200	6.13
Iron	0	5.86
	100	6.44
	200	7.04
Manganese	0	5.88
Molybdenum	60	6.22
Nickel	0	6.06
	100	6.66
	200	7.25
Phosphorus (yellow)	9	5.5
	—7	5.7
	100	6.72
Sulphur (rhombic)	15	5.5
	48	5.64
,, (monoclinic)	15	5.7
	26	5.80
Silicon	0	4.87
	100	5.24
	200	5.60
Tungsten	60	6.24
Vanadium	50	5.88

TABLE X.—*Atomic Heat of Carbon.*

Variety.	Temperature, ° C.	Atomic Heat, cal./g. atom/° C.
Diamond	20	1.45
	50	1.75
	100	2.26
	200	3.23
	250	3.59
Graphite	20	2.00
	50	2.26
	100	2.66
	150	3.01
	200	3.33
	250	3.61

TABLE XI.—*Atomic and Specific Heats of Elements at 100° C.*

Element.	Atomic Weight.	Atomic Heat.	Specific Heat.
Aluminium .	26.97	6.05	0.224
Arsenic (mean) .	74.91	6.33	0.084 ₅
Chromium .	52.01	5.82	0.112
Copper .	63.57	5.98	0.094
Manganese .	54.93	6.48	0.118
Molybdenum .	95.95	6.52	0.068
Nickel .	58.69	6.66	0.113
Phosphorus (red)	30.98	6.72	0.217
Sulphur (mean) .	32.06	6.18	0.193
Silicon .	28.06	5.24	0.187
Tungsten .	183.9	6.26	0.034
Vanadium .	50.95	6.11	0.120

From the analyses given in Table I. the heat capacity of the aluminium, arsenic, chromium, copper, manganese, molybdenum, nickel, phosphorus, sulphur, silicon, tungsten, and vanadium present in each steel was calculated, using the values in Table XI. The total heat capacity of these elements was then subtracted from the heat capacity of 100 g. of the steel, as given by the specific-heat experiments, the remainder being due to the carbon and iron present. This result is given in the fourth column of Table XII.

TABLE XII.—*Calculated Heat Capacity at 100° C. of Carbon and Iron in 100 g. of Steel.*

Steel.	Wt. of Carbon, g.	Wt. of Iron, g.	Heat Capacity of Carbon and Iron Together, cal./° C.	
			By Subtracting Contributions of Other Elements.	By Calculation, assuming Specific Heats of C = 0.306 cal./g./° C. a-Fe = 0.1168 cal./g./° C. γ-Fe = 0.1240 cal./g./° C.
1	0.06	99.27	11.57	11.61
2	0.08	99.28	11.60	11.62
3	0.23	98.71	11.62	11.60
5	0.415	98.55	11.61	11.64
6	0.435	98.43	11.59	11.63
7	0.80	98.39	11.81	11.73
101	0.84	98.73	12.09	11.79
8	1.22	97.89	11.78	11.80
4	0.23	97.79	11.33	11.49
9	0.325	95.07	11.15	11.20
10	0.33	94.56	11.32	11.14
11	0.325	94.49	11.56	11.14
12	0.34	94.02	11.17	11.08
19	0.315	97.45	11.67	11.48
20	0.35	97.29	11.33	11.47
21	0.485	95.68	11.44	11.32
13	1.22	85.30	10.97	10.95
14	0.28	70.23	8.55	8.81
15	0.08	70.93	9.05	8.81
16	0.13	86.20	9.93	10.11
17	0.27	84.95	9.80	10.00
18	0.715	74.73	8.60	8.95

experiment, and low enough to avoid disturbances due to peaks in the curves.

The results of other calculations of the same quantity but based on the amounts of iron and

carbon present and on assumed values for the specific heats of these constituents, are given in the last column of Table XII. The values of specific heat selected as being most satisfactory were 0.306 cal./g./° C. for carbon, 0.1168 for iron in the α -form and 0.1240 in the γ -form.

The atomic heat of carbon derived in this way is thus 3.68, and of α - and γ -iron, 6.52 and 6.93, respectively. The value for α -iron is thus higher by about 1% than that given in Table IX. The value for carbon is higher than that for either diamond or graphite, suggesting that in the combined form the element has an atomic heat nearer to the normal value for most elements. The degree to which a calculation on a similar basis reproduces the specific heats of the 22 steels at 100° C. is shown in Fig. 5, where the calculated and observed values are compared. The calculated values in general agree with those obtained by observation to within about 2%, which is well within the uncertainties of the values assumed in the calculation. The calculated value for the tungsten steel (18) is between 3 and 4% high;

it would be reduced without affecting the values for any of the other steels if lower values than those

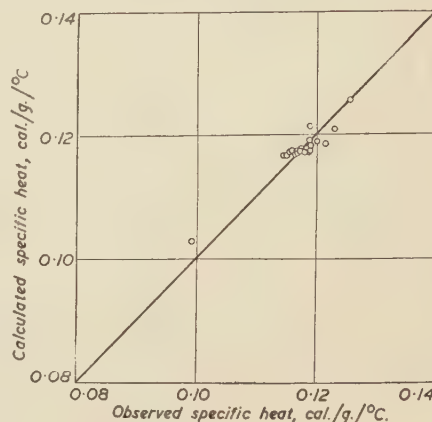


FIG. 5.—Comparison between Observed and Calculated Specific Heats of Steels at 100° C.

given in International Critical Tables were assumed for both tungsten and vanadium.

Section IB.—Specific Heat up to about 1300° C.

By P. R. PALLISTER, B.Sc.

For measuring specific heat at temperatures up to 1300° C., a method utilizing samples of steel in the form of $\frac{1}{4}$ -in. ground rods was adopted. The method involved heating the steel in a furnace to a steady temperature, delivering a known quantity of electrical energy by the passage of a heavy current of short duration, and observing the final temperature. The quantity of energy delivered was derived from measurements of the electrical resistance of the rod and the strength and duration of the current. Temperature measurements were made by thermocouples calibrated in the Laboratory in terms of the International Temperature Scale.

APPARATUS.

Diagrams of the apparatus and of its electrical circuit are shown in Figs. 6 and 7, respectively.

The furnace comprised an alumina tube, 30 in. long, $1\frac{1}{2}$ in. internal dia., and $\frac{1}{4}$ -in. wall thickness, wound with Kanthal strip, $\frac{1}{4} \times 0.002$ in., and supported centrally in a 6-in. dia. steel cylinder, the space between them being filled with powdered alumina for thermal insulation. The cylinder carried at the upper end a flange to which the steel lid could be bolted, and the joint was made air-tight by the insertion of a rubber gasket. By immersing the body in a tank of running water and circulating water through a coil soldered to the lid, the outer surfaces of the furnace were

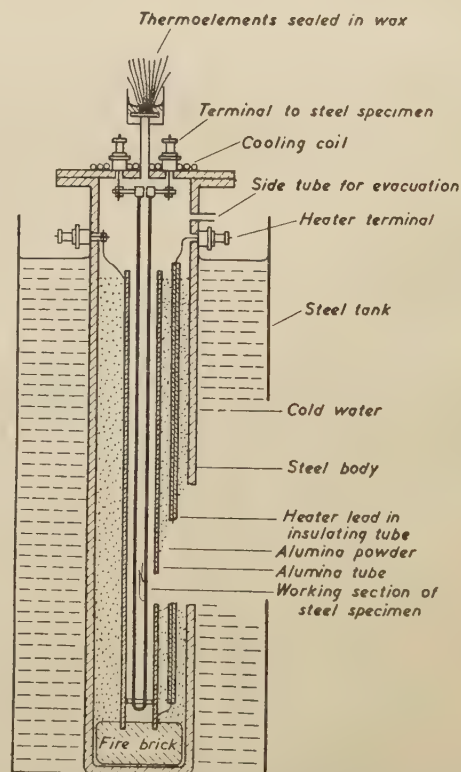


FIG. 6.—Apparatus for Determining Specific Heats up to 1300° C.

kept cool. A side tube leading from the upper end of the furnace body connected with a rotary

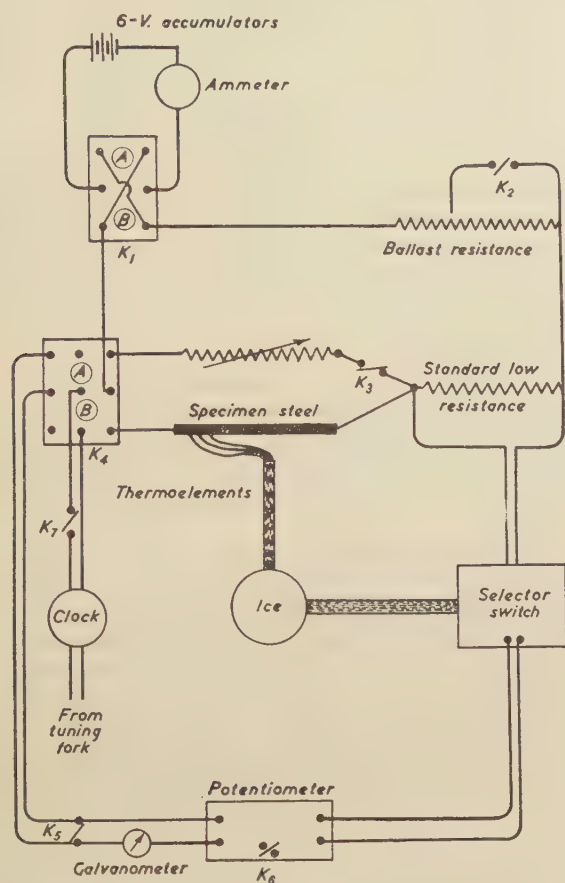


FIG. 7.—Electrical Circuit of Apparatus.

oil pump and a vacuum gauge. Leads from the furnace winding emerged *via* adapted sparking plugs which were rendered air-tight by a film of shellac. Two other plugs screwed into the lid carried the polished steel rod under test. This rod was of U form, having been bent under the influence of heat applied to the centre of the rod whilst the adjoining parts were kept cold. The two parallel arms of the test-rod, each 30 in. in length, passed down into the furnace tube and were anchored symmetrically at the lower end by means of a disk of steatite. Thermocouples were welded to the rod at certain positions, and the leads, insulated by fireclay tubing, passed out of the furnace through a perforated disk of steatite which was sealed with wax. Power for the furnace was supplied from a transformer and was capable of continuous control by a rheostat in the primary circuit. The maximum requirement was less than 1 kW.

A 6-V. battery of 450-amp. hr. capacity served as a source of the energy which had to be imparted rapidly to the rod. Another circuit, however, the

resistance of which was always adjusted to equal that of the rod circuit, was used to steady down the output of the battery before changing over to the main circuit. For measuring rod resistances the circuit included a standard low resistance, the potential difference across which was compared with that across the working section of the rod when passing a small current. Two of the thermoelements welded to the rod were used as potential leads for this purpose. Both Chromel/Alumel and platinum/13% rhodium-platinum thermocouples were used during the course of the investigation.

Timing of the passage of the current through the rod was accomplished by clockwork mechanism connected to a phonic wheel which in turn was fed from and synchronized with a standard tuning fork. The instrument carried dials reading to $\frac{1}{100}$ sec.

Temperature and resistance measurements were carried out using a Vernier potentiometer and a galvanometer of period 1 sec.

EXPERIMENTAL DETAILS.

In order to follow out the method which has already been stated in principle, certain conditions had to be complied with :

- (a) The working length of the specimen steel had to be at a uniform temperature when in thermal equilibrium with the furnace;
- (b) the temperature increment on delivery of the electrical energy had to be small; and
- (c) the energy had to be delivered rapidly, followed by rapid observations of the temperature.

For true specific-heat measurement in regions where it is variable (a) and (b) were necessary; (b) and (c) were necessary and became of increasing importance with rising temperature on account of the cooling of the rod by radiation.

A preliminary exploration, therefore, of the temperature distribution along the steel rod was made under steady conditions at various power consumptions of the furnace. Before heating the furnace, the whole length of the rod would, of course, be at a constant temperature. At the highest temperature, 1350° C., the most uniform section of the rod was found to vary by 4½° C. over a length of 10 cm. Intermediate stages of heating revealed roughly proportional effects. It was decided to confine the measurements to a 5-cm. length which involved a maximum variation of 2° C. at the highest temperature. This length was defined by the positions of two similar thermoelements which served as potential leads for resistance measurements, the principal thermocouple being welded to the rod halfway between them. The possibility that the thermocouple contact on the rod would disturb by conduction the normal temperature increment at the point of contact

was also investigated using both the base-metal thermocouples of 26 S.W.G. and the platinum/13% rhodium-platinum thermocouples of 0.3 mm. dia. Measurements of the specific heat of a certain steel were made using single-wire junctions and also junctions made with wires doubled back so as to have twice the area of contact on the rod and double the cross-sectional area of conductor, the free ends being twisted around the main thermocouple leads. No effect could be detected in the results. The Chromel/Alumel thermocouples functioned satisfactorily up to about 1150° C. but failed rapidly thereafter, presumably through accelerated diffusion of the constituent elements in solid solution both in the thermoelements and in the steel. The platinum thermocouples survived for longer periods but always needed replacement before the whole temperature range on a certain steel had been completed. Rewelding the thermocouples after removing the last inch restored the system to its original efficiency, and previous observations could for a time be repeated. To effect the replacement of the thermocouples it was necessary to allow the furnace and steel rod to cool down, but consideration is given to this matter further on. During some measurements an additional platinum/rhodium-platinum thermocouple was installed in a gas-tight sheath of pythagoras, the junction lying just above the working section of the rod. This thermocouple acted as a control, in that comparative measurements of temperature made under static conditions could be repeated as desired to guard against errors due to incipient contamination of the couples exposed in the furnace. Such a process involved cooling the furnace occasionally in the course of a series of measurements in order that the comparison might be made at a lower temperature where original freedom from contamination could be assumed. However, it was much quicker to proceed with

the specific-heat measurements progressively with rising temperature without using the control thermocouple, but repeating a measurement occasionally in order to detect any error due to contamination. The onset of contamination was revealed by a higher value of apparent specific heat and successive results rapidly deviated.

The heating current flowing in the rod varied from 75 to 200 amp. and lasted for 2 or 3 sec. Such a time interval was sufficiently long to allow a sensibly steady ammeter reading to be taken. Under these conditions the increment in temperature was about 5° C., although smaller increments were frequently employed.

The reliability of the clock was established by repeating specific-heat observations at a certain temperature with varying heating periods.

All the measurements were done *in vacuo*, the pressure being maintained at 0.01 mm. of mercury, and no trouble was experienced by oxidation of the steel rods, the thermocouples, or the furnace winding.

The following procedure was therefore adopted in carrying out a typical experiment, assuming steady thermal conditions to have been attained : First, a resistance measurement was made on the rod, the potential drop across the working section being measured both before and after reversal of a small current through it in order to eliminate any thermal e.m.f. present in the circuit. The temperature was again noted and the potentiometer reading advanced by an amount corresponding to the approximate temperature increment anticipated. After passing a heavy current momentarily through the alternative circuit, the current was diverted abruptly to the circuit through the test-specimen for a few seconds by a special composite switch, which also operated the clock; the ammeter reading was noted and the current cut off, the same switch simultaneously stopping the clock and closing the galvanometer

TABLE XIII.—*Mean Specific Heat of Carbon Steels over 5° C. Ranges (cal./g./° C.).*

Mean Temp., ° C.	Steel.							
	1.	2.	3.	5.	6.	7.	101.*	8.
850	0.154	0.148	...	0.148
900	0.157	0.156	0.155	0.148	0.150	0.148	0.148	0.148
950	0.159	0.156	0.155	0.149	0.150	0.150	0.147	0.149
1000	0.160	0.157	0.155	0.150	0.150	0.152	0.148	0.151
1050	0.160	0.157	0.155	0.151	0.150	0.154	0.151	0.153
1100	0.160	0.158	0.156	0.152	0.152	0.157	0.154	0.154
1150	0.160	0.158	0.158	0.154	0.155	0.159	0.158	0.156
1200	0.160	0.159	0.160	0.158	0.158	0.161	0.161	0.158
1250	0.160	0.159	0.163	0.162	0.161	0.162	0.164	0.160
1300	...	0.159	0.166	0.166	0.164	0.163

* The analysis of this sample was stated to be : C 0.85%, Si 0.15%, Mn 0.31%. For all other steels, see the analyses given in Table I.

TABLE XIV.—*Mean Specific Heat of Alloy Steels over 5° C. Ranges (cal./g./° C.).*

Mean Temp., ° C.	Steel.							
	4.	9.	10.	11.	12.	19.	20.	21.
850	0.139	0.148
900	0.140	0.156	0.150	0.149	0.155	0.148	0.141	0.150
950	0.142	0.155	0.151	0.151	0.153	0.149	0.143	0.151
1000	0.144	0.154	0.152	0.153	0.151	0.150	0.145	0.153
1050	0.146	0.153	0.153	0.155	0.151	0.149	0.146	0.155
1100	0.148	0.153	0.154	0.156	0.152	0.148	0.148	0.157
1150	0.150	0.154	0.155	0.157	0.153	0.148	0.151	0.159
1200	0.151	0.156	0.156	0.158	0.154	0.150	0.152	0.161
1250	0.153	0.157	0.157	0.159	0.155	0.153	0.154	0.163
1300	0.155

circuit of the potentiometer system. Observations of the small out-of-balance galvanometer deflections were made over a period of 2 min. to afford a means of extrapolation backwards to the time of cessation of heating and of making a correction for heat loss during the heating period.

DISCUSSION OF RESULTS.

Measurements are considered to be accurate to about $\pm 4\%$. The bulk of the error arises from

TABLE XV.—*Mean Specific Heat of High-Alloy Steels over 5° C. Ranges (cal./g./° C.).*

Mean Temp., ° C.	Steel.			
	15.	16.	17.	18.
850	0.158
900	0.156	0.153	0.156	0.138
950	0.155	0.155	0.155	0.140
1000	0.156	0.156	0.154	0.144
1050	0.157	0.156	0.153	0.147
1100	0.158	0.156	0.155	0.146
1150	0.160	0.155	0.156	0.146
1200	0.161	0.155	0.158	0.146
1250	0.162	0.155	0.160	0.146

loss of heat by radiation from the test-rod when its temperature is raised above its initial steady value, the correction necessary on this account

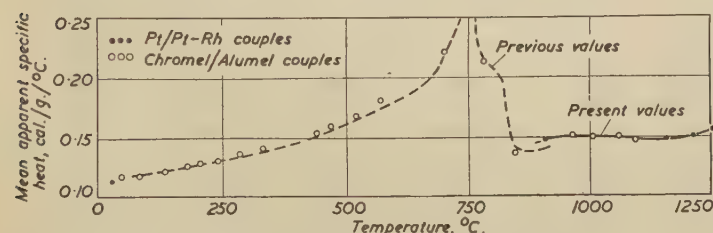


FIG. 8.—Specific Heat of Steel 19.

amounting to about 10% at 1300° C. (It is of incidental interest to record here that at this

temperature the observed rate of loss of heat points to an emissivity of about 0.6.)

Results given in Tables XIII.–XV. cover measurements of specific heat from 900° C. to at least 1250° C. In addition, to enable a comparison to be made with data obtained by the earlier method, all the steels have been investigated at room temperature and several at intermediate temperatures up to 900° C. Results at room temperature were all comparable with the values reported earlier and need no further comment. Steel 19, selected at random from the series, yielded results from room temperature up to 900° C. which fell satisfactorily upon the curve plotted from data given in the earlier work, as will be seen in Fig. 8. In this figure the curve was derived from the stated values of mean apparent specific heat over 5° C. ranges, except in the neighbourhood of the Curie point where values related to 5° C. ranges. Further comparison between the previous and present results on all the steels was secured at about 900° C. where the two methods overlapped. Only in the case of steel 14 was there a serious discrepancy (10%) and hence measurements were made over the whole range from room temperature upwards. A considerable number of observations were taken necessitating six separate furnace heatings, and before the last series of measurements, the steel rod was heated to 950° C. in air and cooled in water so that it might start in the same state as when supplied. All the values obtained lie fairly well on a single curve so that the discrepancy alluded to cannot be explained by thermal hysteresis. Since the new curve is everywhere higher than the original, except at room temperature where they blend, the specific heats for this steel are given separately over the complete range of temperature in Table XVI. Steel 13 was also measured in some detail in order to meet the deficiency of data from 500° C. upwards; these values of specific heat are included in Table XVI.

TABLE XVI.—*Mean Specific Heat of High-Alloy Steels over 5° C. Ranges (cal./g./° C.).*

Mean Temp., ° C.	Steel.		Mean Temp., ° C.	Steel.	
	13.	14.		13.	14.
0	0.118	0.117	650	0.153	0.141
50	0.122	0.119	700	0.154	0.140
100	0.126	0.121	750	0.155	0.140
150	0.132	0.123	800	0.156	0.140
200	0.137	0.126	850	0.158	0.141
250	0.141	0.129	900	0.159	0.142
300	0.144	0.131	950	0.160	0.143
350	0.145	0.130	1000	0.162	0.143
400	0.146	0.129	1050	0.163	0.143
450	0.147	0.133	1100	0.165	0.145
500	0.148	0.137	1150	0.166	0.147
550	0.183	0.139	1200	0.167	0.151
600	0.154	0.141	1250	0.168	0.154

Carbon steels 2, 3, 5, 6, 7, and 8 and the 1½% manganese steel (4) were old samples originally used for linear-expansion measurements up to 1000° C., whilst the remainder of the series tested comprised new samples that were received in the course of the work. The question arises whether the specific-heat measurements on the steels in the first category were influenced by their thermal history subsequent to being supplied for test. The same factor, moreover, must be considered in relation to all the steels on account of their having been subjected to alternate heating and cooling during the investigation. To meet this query it may be assumed that, at the high temperatures with which this paper is mainly concerned, equilibrium in constitution would be rapidly attained and any transformation which may occur would do so without appreciable lag.

It is to be noted that, in order to survey as quickly as possible the temperature range hitherto unexplored, observations have been made sometimes as much as 50° C. apart and therefore the measurements of mean specific heat over the small

ranges involved, *i.e.*, about 5° C., leave a considerable portion of the temperature scale not actually investigated. Only in the absence of structural transformations in the steels at the temperatures concerned would there be justification for interpolating between the observed points. The location of any such transformations is therefore important. The actual observations made certainly do not reveal any noticeable discontinuities for any of the steels at these high temperatures, nor would the known constitution of simple alloy systems lead one to expect them in general in this temperature range. Steels 16, 17, and 18 might be exceptions to the latter generalization and, furthermore, the presence of additions and impurities in all the steels may slightly modify the constitution diagrams and give rise to corresponding small thermal changes. Thermal analysis of this series of steels, carried out by Jenkins, Bucknall, and Jenkins,³ reached 960° C. and as high as 1500° C. in the case of steel 18. A communication from the Metallurgy Division of the National Physical Laboratory states that the work on steels 16 and 17 has now been extended to 1300° C. Steels 16 and 17 were reported to have shown only a "minor" change at 926° C. and 911° C., respectively, and the present communication shows a "doubtful" absorption of heat over a range of 50–100° C. at higher temperatures. Any such long-range absorption of heat would be taken account of in Table XIX. Steel 18 was reported to show an arrest, described as either "minor" or "small," in the heating curves at about 1150° C. The effect on specific-heat measurements is not appreciable, for numerous contiguous observations have been made on this particular steel between 1125° and 1175° C. without finding an appreciable departure from neighbouring observations. It may therefore be concluded that for each steel of this series it is not unreasonable to link up the observed specific-heat values by a smooth curve. Observations were actually made very near to the rational temperatures, 900° C.,

TABLE XVII.—*Total Heat of Carbon Steels—Initial Temperature 50° C. (cal./g.).*

Temp., ° C.	Steel.							
	1.	2.	3.	5.	6.	7.	101.	8.
50	0	0	0	0	0	0	0	0
900	141	142	142	137	142	144	147	144
950	148	150	150	144	150	151	154	151
1000	156	158	158	152	157	158	162	158
1050	164	165	165	159	165	166	169	166
1100	172	173	173	167	172	174	177	174
1150	180	181	181	174	180	182	184	182
1200	188	189	189	182	188	190	192	189
1250	196	197	197	190	196	198	201	197
1300	..	205	205	198	204	206

TABLE XVIII.—*Total Heat of Alloy Steels—Initial Temperature 50° C. (cal./g.).*

Temp., ° C.	Steel.							
	4.	9.	10.	11.	12.	19.	20.	21.
50	0	0	0	0	0	0	0	0
900	136	140	139	138	144	139	140	139
950	143	148	146	145	151	147	147	147
1000	150	156	154	153	159	154	154	155
1050	158	163	162	161	167	162	161	162
1100	165	171	169	169	174	169	169	170
1150	172	179	177	177	182	177	176	178
1200	180	186	185	185	190	184	184	186
1250	187	194	193	193	197	191	191	194
1300	195

TABLE XIX.—*Total Heat of High-Alloy Steels—Initial Temperature 50° C. (cal./g.).*

Temp., ° C.	Steel.			
	15.	16.	17.	18.
50	0	0	0	0
900	120	135	140	114
950	128	143	147	121
1000	136	151	155	128
1050	144	159	163	135
1100	152	166	171	143
1150	160	174	178	150
1200	168	182	186	157
1250	176	190	194	164

TABLE XX.—*Total Heat of High-Alloy Steels—Initial Temperature 50° C. (cal./g.).*

Temp., ° C.	Steel.		Temp., ° C.	Steel.	
	13.	14.		13.	14.
50	0	0	700	94.7	84.5
100	6.2	6.0	750	102	91.4
150	12.6	12.1	800	110	98.5
200	19.4	18.3	850	118	106
250	26.3	24.7	900	126	113
300	33.4	30.2	950	134	120
350	40.7	36.7	1000	142	127
400	48.0	43.2	1050	150	134
450	55.3	49.8	1100	158	142
500	62.7	56.5	1150	167	149
550	71.0	63.4	1200	175	156
600	79.4	70.4	1250	183	163
650	87.1	77.5			

950° C., &c., at which values are given in the Tables.

Total heats from 50° C. are given in Tables XVII. to XX., which follow on in general from the tabulated results previously reported.¹ The figures for steels 13 and 14, however, are entirely independent since fresh values of specific heat have now been obtained from room temperature upwards.

In order to correlate graphically the specific-heat data with similar data published by other workers, use has been made of the approximation that at any one temperature all the constituent atoms of the metals examined would have the same thermal capacity. A linear relation would then be expected to hold between the number of atoms in a certain mass of metal and the specific heat. There are known to be restrictions to the validity of such an assumption for ordinary temperatures in that even elementary substances show variations in atomic heat. Furthermore, the phenomenon of allotropy either in elements or compounds is associated with a diversity of specific heat. At high temperatures the divergences may be smaller; carbon certainly tends towards more normal values. Fig. 9 has been drawn from observations made at 1250° C., at which temperature heats of transformation are unlikely to influence the measured values of specific heat. The scale of abscissæ is derived from the summation of m/A for each constituent element, where m is the mass of element per 100 g. of metal and A is the atomic weight.

Multiplying $\Sigma m/A$ by the Avogadro number 6.02×10^{23} gives the number of heterogeneous atoms per 100 g. of metal. It will be seen that the observation points are dispersed bilaterally about the ordinate which marks the position of iron, an element of high atomic weight, such as tungsten, contributing less to the specific heat than an element such as carbon. A straight line is drawn to pass through the origin of co-ordinates and the present data. Departures in specific heat from the linear relation are less than 4%. The observation points for the carbon steels appear to predict a specific heat for iron at about 0.160 cal./g./° C., but it is hoped that new determinations of the specific heat of high-purity iron will shortly be available. Zuithoff⁴, working on a series of iron-nickel alloys, obtained data which fit the graph reasonably well. His estimated value for iron is 0.152. Jaeger⁵ and his collaborators get

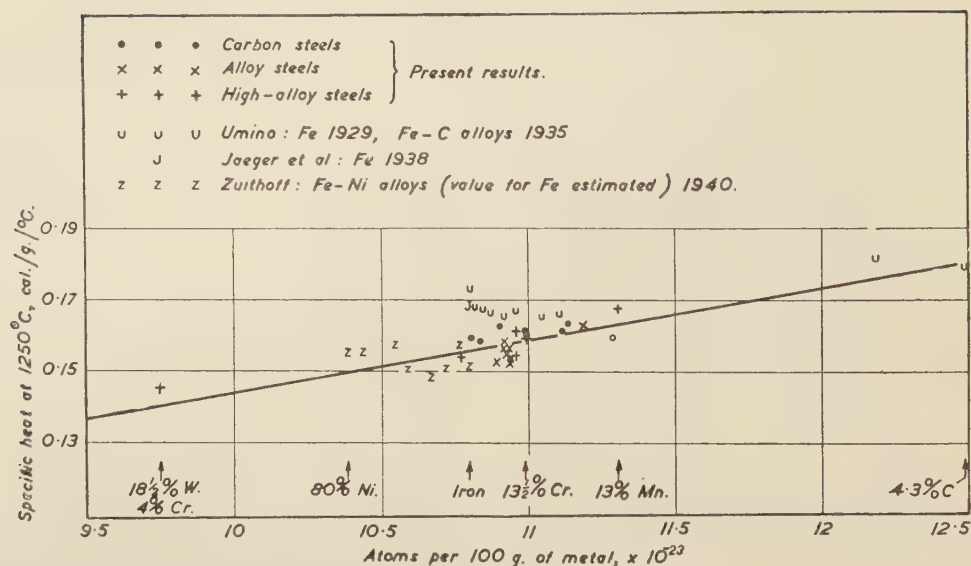


FIG. 9.—Specific Heat Plotted against Number of Atoms at 1250° C.

a higher value for electrolytic iron, *viz.*, 0.169. Umino⁶ finds a higher value still for electrolytic iron. His data on iron-carbon alloys⁷ are, in general, well above the present results, particularly in the case of the low-carbon alloys, but two of his observation points on high-carbon alloys relating to the liquid state support the trend of the graph. Bearing in mind the limitations of this means of correlating specific-heat measurements made on

different materials, it may be noted that elements conforming to the straight-line graph of Fig. 9 would have an atomic heat at 1250° C. of 8.73 cal./° C.

ACKNOWLEDGMENT.

The development of this investigation followed initial trials made by J. H. Awbery, B.A., B.Sc., and A. R. Challoner.

Section II.—Expansion Coefficients up to 1000° C.

BY G. G. SHERRATT, B.A., ASSISTED BY A. R. CHALLONER.

The present section gives the coefficients of expansion of fourteen alloy and high-alloy steels. The same apparatus was used for the determination of the coefficients of expansion of these steels as for the previous group of carbon steels. The rate of heating of the specimens was 3–4° C./min. Steel 12 was tested first as received and again after being subjected to the following heat-treatment: Maintained at 650° C. for 3 hr., then cooled to room temperature at a rate of approximately 200° C./hr.

The data obtained are given in Figs. 10, 11, and 12 and in Tables XXI.–XXIV.

In Figs. 10 and 11 the values of $(L_t - L_0)/L_0$ are plotted against temperature in the region of transformation. Fig. 12 shows the expansions of steels 13, 14, and 15 over the entire range of temperature covered.

In Tables XXI. and XXII., the mean coefficients of expansion of the alloy steels and the high-alloy steels, respectively, are given. The data in Table XXIII. are for steel 12 before and after heat-

treatment. Table XXIV. gives the percentage decrease in length at room temperature produced by heating the steels to about 1100° C. in the course of the tests.

A study of the data obtained in this investigation reveals the following features:

(1) Fig. 10 shows that steels 9, 10, 11, and 12 behave similarly throughout the temperature range. In chemical composition they have approximately the same amounts of nickel, manganese, and carbon, so the variations in the chromium and molybdenum contents appear to be of small importance as regards the expansion coefficient. The change in dimensions on passing through the transformation point is practically the same in all the steels.

(2) Another group which gave similar results is that containing steels 19 and 20. These steels differ in nickel and molybdenum content but have the same carbon and chromium content. The essential difference between the composition of this group and that of the preceding one is

the much smaller nickel content of steels 19 and 20.

(3) Steel 21, which has a high silicon content, shows an appreciably smaller decrease in length at

covering the range 430–550° C. and the second 930–1040° C., where there are departures from the smooth curve connecting length and temperature. These are not found in the curves of the other high-alloy steels.

(5) It will be seen from Table XXII. that the coefficient of expansion of steel 13 (a 13% manganese steel) is greater than those of the other steels in the series.

(6) Steel 14, which was supplied in the quenched state, shows no variation in the expansion coefficients in the normal transformation temperature region (see Fig. 12), whereas in the specific-heat/temperature curve there is evidence of small absorption of energy in this region. As the steel

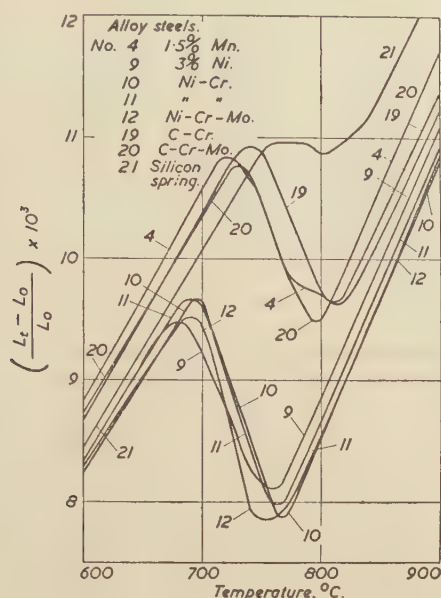


FIG. 10.—Expansion of Alloy Steels in Neighbourhood of Change Points.

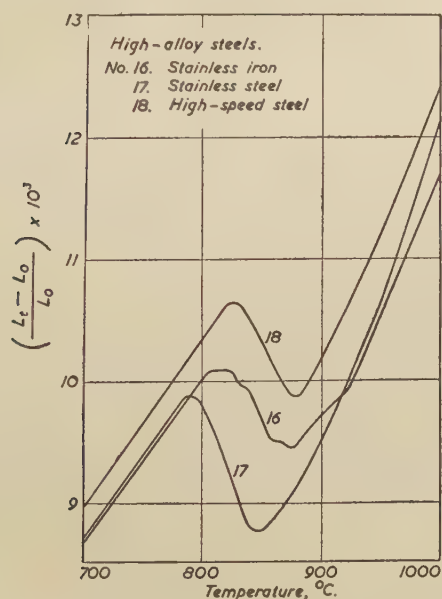


FIG. 11.—Expansion of High-Alloy Steels in Neighbourhood of Change Points.

the transformation point than the other members of the alloy-steel group.

(4) Fig. 12 shows that for steel 13 there are two well-defined temperature intervals, the first

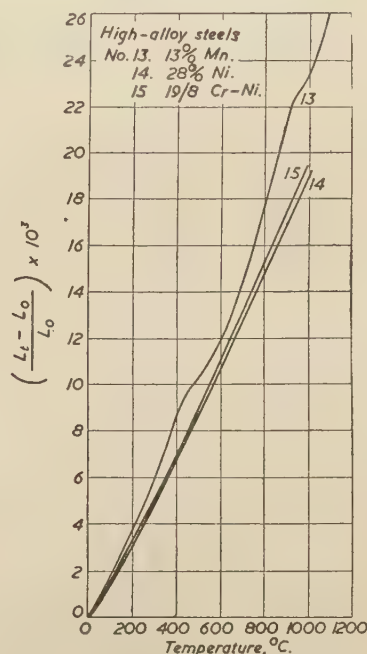


FIG. 12.—Expansion-Temperature Curves for Steels 13, 14, and 15.

in the quenched state is raised in temperature and the transformation region is approached, some of the material may change from the γ - to the α -state so that when the transformation point is reached, absorption of energy due to the transformation back to the γ -state would be observed. It is conceivable that the small amounts of energy liberated or absorbed during these partial changes would affect the specific-heat curve without being apparent in the dimensional-change curve.

(7) The data given in Table XXIII. show that the coefficient of expansion of steel 12 below the transformation point was not materially affected by the heat-treatment, but that the coefficient is increased at higher temperatures, from 700° C. upwards. The length decreased slightly during

TABLE XXI.—*Mean Coefficients of Thermal Expansion of Alloy Steels.*

Temp. Interval, ° C.	Steel.							
	4.	9.	10.	11.	12.	19.	20.	21.
	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$
0- 100	11.89	11.20	11.36	11.45	11.63	12.16	12.67	11.19
0- 200	12.68	11.80	12.29	12.15	12.12	12.83	13.11	12.21
0- 300	13.36	12.36	12.82	12.72	12.61	13.32	13.47	12.90
0- 400	13.87	12.90	13.18	13.20	13.12	13.72	13.82	13.35
0- 500	14.33	13.46	13.44	13.62	13.50	14.08	14.19	13.73
0- 600	14.72	13.87	13.72	13.93	13.79	14.46	14.55	14.09
0- 700	15.11	13.10	13.73	13.70	13.45	14.81	14.83	14.41
0- 800	12.11	11.10	10.69	10.87	10.67	12.13	11.92	13.59
0- 900	12.47	12.32	12.04	12.15	11.99	12.64	13.01	13.74
0-1000	13.67	13.29	13.11	13.17	12.96	13.66	13.86	14.54
0-1100	...	14.08	13.95	14.02	13.62	14.44	14.48	15.29

TABLE XXII.—*Mean Coefficient of Thermal Expansion of High-Alloy Steels.*

Temp. Interval, ° C.	Steel.					
	13.	14.	15.	16.	17.	18.
	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$
0- 100	18.01	13.73	14.82	10.13	9.98	11.23
0- 200	19.37	15.28	16.47	10.66	10.65	11.71
0- 300	20.71	16.32	17.11	11.14	11.13	11.98
0- 400	21.71	17.02	17.61	11.54	11.50	12.20
0- 500	20.76	17.46	18.04	11.85	11.83	12.41
0- 600	19.86	17.82	18.43	12.15	12.20	12.62
0- 700	20.49	18.07	18.77	12.37	12.46	12.79
0- 800	21.86	18.28	19.03	12.56	12.16	12.97
0- 900	23.45	18.55	19.21	10.79	10.57	11.35
0-1000	23.13	18.83	19.36	11.70	12.18	12.44
0-1100	23.61	12.68	13.60	13.34

TABLE XXIII.—*Results of Two Experiments on Steel 12.*

Temp. Interval, ° C.	Mean Coefficient of Thermal Expansion $\times 10^6$.	
	As Received.	After Heat-Treatment.
0- 100	11.63	11.54
0- 200	12.12	12.06
0- 300	12.61	12.58
0- 400	13.12	12.97
0- 500	13.50	13.49
0- 600	13.79	13.81
0- 700	13.45	13.93
0- 800	10.67	11.24
0- 900	11.99	12.52
0-1000	12.96	13.50
0-1100	13.62	14.26

the heat-treatment, the change being of the order of 1 part in 4000 or 0.025%. After the second experiment a further decrease in length was observed; this amounted to 0.136% and compares with 0.172% in the first experiment (see Table XXIV.).

(8) It has been suggested that some of the physical properties of iron alloys are a function of the composition when the other elements present in the steel are expressed as atomic percentages. In the case of the coefficients of expansion of these steels between 0° and 300° C. there is a rough correlation with the total amounts of the elements present, other than iron, when expressed as atomic percentages, the exceptions being steels 13, 14, and 15, which are in the γ -state.

TABLE XXIV.—*Change in Length after Test.*

Steel.	4.	9.	10.	11.	12.	13.	14.	15.	16.	17.	8.	19.	20.	21.
Decrease, %.	0.022	0.064	0.122	0.113	0.172	0.076	0.020	0.015	0.032	0.011	0.122	0.080	0.095	0.070

Section IIIA.—Electrical Resistivities up to 1300° C.

By R. W. POWELL, D.Sc., F.Inst.P., ASSISTED BY M. J. HICKMAN.

The first report⁸ contained results for the electrical resistivities of twenty-one of the steels up to temperatures which varied from 150° to 350° C. These measurements, which were made in the course of a determination of thermal conductivity by a method in which a gradient in temperature was set up from end to end of a 1-in. dia. bar of steel, were included primarily so as to furnish information on the relation between the thermal conductivity and electrical resistivity. The presence of a gradient of temperature in the specimen, however, reduces the accuracy with which the variation of a property with temperature can be determined. Although the gradient is unavoidable when thermal conductivity is being measured, this is not so with electrical resistivity and it was considered advisable to carry out separate determinations of this property on specimens maintained at uniform temperatures. In addition, it has been shown⁹ that the thermal conductivity can be derived from a knowledge of the electrical resistivity with greater certainty at high than at low temperatures. It was considered, therefore, that the extension of the electrical-resistivity determinations to temperatures of the order of 1300° C. would enable estimates of the thermal conductivities to be formed to these temperatures, pending their experimental determination. Values estimated in this way are discussed in Section IIID.

The present Section deals with the determination of the electrical resistivities of all the steels detailed in Table I. up to temperatures of just over 1300° C.

The specimens of steel available for the determination were unused lengths cut from those supplied for the work on coefficients of expansion and were in the form of ground rods 5 mm. in dia. and about 60 cm. in length.

In the case of the eutectoid steel, steel 101, the specimen used was a short rod, 0.63 cm. in dia. and 4.1 cm. in length, machined from a piece cut from the block supplied for the specific-heat determination.

APPARATUS AND METHODS FOR DETERMINATIONS UP TO 1300° C.

The measurements to high temperatures were at first carried out on batches of four specimens at a time. Steels 15, 16, 17, and 18 composed the first batch, 13, 14, 20, and 21, the second, and 9, 10, 11, and 12, the third. Each of the four rods was cut to a length of 26 cm. and fitted securely into connecting pieces of tool steel 3.5 cm. in

length, so that the test-rods were connected in series and formed the long sides of a framework having the approximate form of a 3 × 26-cm. rectangular parallelepiped. Current could be led into the rods by means of two extension rods of steel. Two butt-welded thermocouples composed of No. 26 S.W.G. Chromel and Alumel wires were electrically welded to the centre section of each test-rod at points about 10 cm. apart, the wires being set with their lengths perpendicular to the axis of the rod. These thermocouples served to measure the temperature of the rod and were also used as potential leads. The specimens were

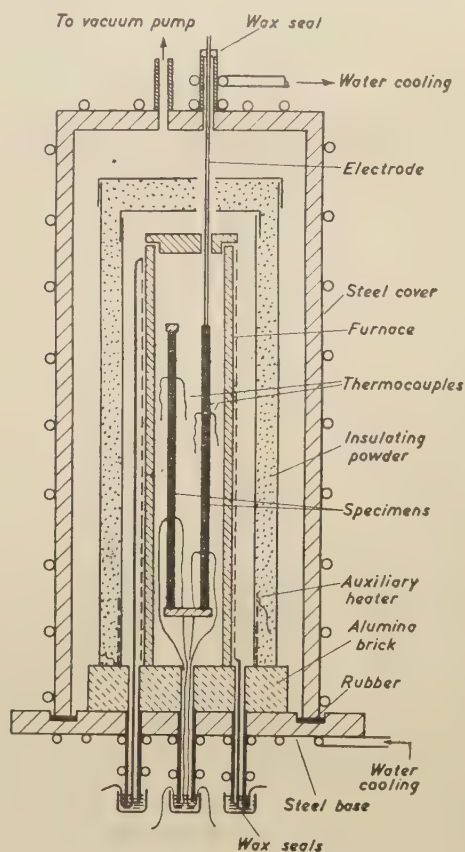


FIG. 13.—Apparatus for Electrical-Resistivity Determinations up to 1300° C.

mounted within a vertical furnace as shown in Fig. 13. The thermocouples were insulated by fireclay tubing and brought out through wax seals at the base of the apparatus. The two electrodes projected through the top of the steel outer cover, where they were waxed in position and served to support the specimens. The furnace, which consisted of a pythagoras tube,

35 cm. in length and 7 cm. internal dia., wound with $\frac{3}{16}$ -in. wide resistance tape of an alloy known commercially as Kanthal, stood on an insulating base of alumina and was surrounded by radiation shields packed with a heat-insulating powder. A second heating coil was provided to supply heat to the base of the furnace and by suitable adjustment of the energy dissipated in this heater it was possible to neutralize any temperature gradient over the working sections of the rods. The whole apparatus stood on a water-cooled steel base, and was surrounded by a water-cooled steel cover. The joint between this cover and the steel base was effected by a thin rubber ring and was waxed, so that the whole enclosure could be evacuated.

In carrying out the experiment the apparatus was exhausted to a pressure of about 0.1 mm. of mercury and the specimens were heated uniformly to a series of relatively steady temperatures by increments of about 25° C. At each steady temperature the electrical resistivities of the four rods were measured by connecting the rods in series with a standardized resistance and passing a current of the order of 0.8 amp. through the circuit. Using the thermocouple wires as potential leads the resistance of the centre section of each steel was determined from a comparison of the potential drop across this section of the rod with that across the standard resistance. All observations were made on a potentiometer and, to eliminate thermal e.m.f., measurements were made before and after reversal of the current. The temperature was obtained as the mean of thermocouple observations taken immediately before switching on, and after switching off, the current for the resistivity measurements.

About ten complete sets of observations were obtained each day; the specimens were then maintained over night at, or slightly below, the final temperature attained during the day's run. The next day the tests were recommenced at approximately the same temperature as that reached on the previous day. At times the resistivity was found to have decreased during this interval. In general, this decrease was well under 1%, but with steel 13 the resistivity decreased from 103.4 to 92.0 microhm cm. units whilst held overnight at a temperature of about 470° C.

These results confirmed earlier indications of the occurrence of some change in the properties of steel 13 at about 300° C. and led to a more detailed investigation being made into the dependence of the properties of this steel on time and temperature of heating (*see* Section IIIB.).

Furthermore, it was decided to modify the method of future experiments so that the resistivity determinations could be carried out over the full range of temperature whilst the tempera-

ture was steadily increasing at the rate of approximately 3° C./min. The conditions of heating would then be comparable with those employed for the specific-heat determinations described in Section IA.

The general method of assembly was similar to that described above but differed in that only two specimen rods were included. These were about 15 cm. in length and were connected at their lower ends by means of a short bar of tool steel. As before, two butt-welded Chromel/Alumel thermocouples were welded to the centre section of each test-rod at points about 10 cm. apart, and, in addition, a pair of Chromel wires to serve as potential leads were welded to each rod a short distance inside the section bounded by the thermocouples. In order to obtain the necessary readings as speedily as possible, two potentiometers were used. To one potentiometer were connected the lower thermocouples on each rod and the potential leads from the standard resistance, whilst to the other potentiometer were connected the upper thermocouples and the potential leads from the two rods. By employing two observers it was possible to adopt the following procedure when taking the observations :

- (i) Simultaneous observation of the readings of the upper and the lower thermocouples.
- (ii) Circuit for the resistivity measurements completed and simultaneous observations made of the readings of the potential drop across the working sections of the rod and of the drop across the standard resistance.
- (iii) Direction of current for resistivity measurements and of potentiometer current reversed and readings as in (ii) repeated.
- (iv) Simultaneous observations made of the readings of both thermocouples as in (i).

The data obtained before and after the reversal of the currents were averaged when evaluating the results.

This sequence of observations occupied just under 1 min. during which the temperature increased by about 3° C. on the average. In general a set of observations was commenced at 2-min. intervals and readings were taken on the two rods alternately. In this way, values were obtained of the resistivity of any one steel at temperature intervals of about 12° C.

The above method of continuous heating was used for repeat determinations on steels 13 and 18 and for the resistivity determinations made on steels 1 to 8, 101, and 19, the latter steels being tested in pairs as follows : 1 and 2, 3 and 5, 6 and 7, 101 and 8, 4 and 19.

RESULTS.

Large-scale graphs were plotted of the electrical resistivity against temperature, and smooth curves

TABLE XXV.—*Electrical Resistivities of Steels from 0° to 1350° C. (microhm cm. units).*
(Values uncorrected for dimensional changes of the specimen with temperature.)

(Values uncorrected for dimensional changes of the specimen with temp.)																								
Temp., ° C.	Carbon Steels.										Alloy Steels.										High-Alloy Steels.			
	1.	2.	3.	5.	6.	7.	101.	8.	4.	9.*	10.*	11.*	12.*	19.	20.	21.	13.	13.*	14.*	15.*	16.*	17.*	18.	18.*
0	12.0	13.2	15.9	16.0	17.7	17.0	16.5	18.4	19.7	25.9	25.6	26.5	27.7	20.0	21.1	41.9	66.5	66.5	82.9	69.4	48.6	50.3	40.6	40.6
20	13.0	14.2	16.9	17.1	18.9	18.0	17.6	19.6	20.8	27.1	26.8	28.0	28.9	21.0	22.3	42.9	68.3	68.3	84.2	71.0	50.6	52.2	41.9	41.9
50	14.7	16.0	18.7	18.9	20.7	19.8	19.4	21.6	22.5	28.9	28.5	29.4	30.6	22.7	24.0	44.4	71.1	71.1	86.1	73.6	53.6	54.9	...	43.8
100	17.8	19.4	22.4	22.5	24.2	23.2	22.8	25.2	26.9	32.0	31.7	32.5	33.7	25.9	27.1	47.0	75.7	75.6	91.9	77.6	58.4	59.5	...	50.7
150	21.3	22.4	25.4	25.7	27.3	26.8	26.3	29.0	29.4	35.4	35.1	35.9	37.1	29.3	30.5	49.9	80.2	80.2	94.7	81.5	63.2	64.0	54.5	54.4
200	25.2	26.3	29.2	29.6	31.2	30.8	30.3	33.3	33.3	39.0	38.7	39.5	40.6	33.0	34.2	52.9	84.7	84.7	97.2	88.3	72.4	72.6	62.6	58.5
250	29.5	30.5	33.4	33.7	35.4	35.1	34.6	37.9	37.5	42.9	42.7	43.4	44.6	37.1	38.3	56.4	88.9	88.9	99.6	91.6	76.9	76.9	...	67.1
300	34.1	35.2	38.1	38.7	39.9	39.8	39.2	43.0	42.1	47.0	46.9	47.7	48.7	41.7	42.8	60.1	93.1	93.1	101.8	94.6	81.2	81.1	...	71.8
350	39.3	40.2	43.2	43.8	45.0	45.0	44.3	48.3	47.0	51.6	51.6	52.2	53.2	46.0	47.6	68.5	100.4	100.4	105.8	97.6	85.4	85.3	...	76.5
400	44.8	45.8	48.7	49.3	50.4	50.5	49.8	54.0	52.3	56.7	56.7	57.2	58.2	51.7	52.9	73.4	103.6	103.6	107.7	102.6	93.8	93.5	...	81.5
450	50.9	51.8	54.6	55.3	56.3	56.5	55.7	60.1	58.0	62.1	62.3	63.6	64.6	57.3	58.6	78.8	105.9	105.9	109.5	105.0	98.0	97.5	...	86.9
500	57.5	58.4	60.1	61.9	62.6	62.8	62.2	66.5	64.5	67.9	68.1	69.6	70.6	63.6	64.6	84.7	108.1	108.1	112.2	107.2	102.1	101.5	...	92.2
550	64.8	65.7	68.2	68.9	69.5	69.9	69.2	73.4	71.2	74.4	74.8	75.1	75.8	70.6	71.4	91.1	110.0	109.9	114.7	109.2	106.3	105.4	...	97.9
600	72.5	73.4	75.8	76.6	77.0	77.2	76.7	80.2	78.6	81.4	81.7	82.0	82.5	77.8	78.6	98.1	112.6	112.6	117.5	112.2	103.4	102.4	...	103.7
650	80.7	81.6	83.7	84.4	84.7	85.2	84.3	87.8	86.2	88.6	88.8	89.2	89.4	85.3	86.1	105.7	115.6	115.6	120.4	115.1	110.3	109.3	...	110.2
700	89.8	90.5	92.5	93.2	93.6	93.5	92.7	96.4	94.6	99.2	98.1	99.0	99.4	93.4	94.4	105.7	118.0	118.0	123.0	117.5	112.0	111.0	...	115.9
750	100.3	101.1	103.0	103.7	104.2	104.0	103.0	106.7	104.6	109.6	109.6	109.4	109.6	102.6	105.3	114.2	120.4	120.4	125.0	119.7	115.7	114.4	...	119.2
800	107.3	108.1	109.4	110.1	111.3	111.3	110.3	113.0	110.7	115.5	115.5	115.7	115.7	108.6	111.3	117.3	124.5	124.5	128.8	123.8	119.4	117.3	...	120.9
850	110.4	111.1	112.8	113.4	114.0	113.9	112.9	115.6	113.3	118.0	118.0	118.0	118.0	110.6	113.3	119.6	126.3	126.3	130.8	125.8	121.7	119.3	...	122.3
900	112.4	113.0	114.6	115.2	115.8	115.7	114.7	117.4	115.1	119.8	119.8	119.8	119.8	112.2	114.9	121.1	128.5	128.5	133.0	128.0	123.5	121.4	...	123.6
950	114.2	114.8	116.5	117.0	117.6	117.5	116.5	119.2	116.9	121.6	121.6	121.6	121.6	114.6	117.3	123.7	130.5	130.5	135.0	129.6	124.1	121.6	...	124.9
1000	116.0	116.5	118.1	118.7	119.3	119.2	118.2	120.9	118.6	123.3	123.3	123.3	123.3	116.7	119.4	125.9	132.5	132.5	137.0	131.4	125.7	123.8	...	126.0
1050	117.5	117.9	119.4	120.0	120.6	120.5	119.5	122.2	120.0	124.8	124.8	124.8	124.8	118.0	120.7	126.0	133.5	133.5	138.0	132.4	126.7	125.0	...	126.3
1100	118.9	119.3	120.7	121.3	121.9	121.8	120.8	123.5	121.3	126.0	126.0	126.0	126.0	119.0	121.7	127.1	134.5	134.5	139.0	133.4	127.1	125.7	...	126.6
1150	120.3	120.7	122.0	122.6	123.2	123.1	122.1	124.8	122.6	127.3	127.3	127.3	127.3	120.0	122.7	128.0	135.5	135.5	140.0	134.4	127.6	125.3	...	126.9
1200	121.6	122.0	123.3	123.9	124.5	124.4	123.4	126.1	123.9	128.6	128.6	128.6	128.6	121.1	123.8	129.1	136.5	136.5	141.0	135.4	127.9	125.9	...	127.3
1250	123.0	123.3	124.6	125.2	125.8	125.7	124.7	127.4	125.2	130.0	130.0	130.0	130.0	122.5	125.2	130.5	137.5	137.5	142.0	136.8	128.4	126.3	...	128.0
1300	124.1	124.4	125.7	126.3	126.9	126.8	125.8	128.5	126.3	131.1	131.1	131.1	131.1	123.0	125.7	131.0	138.0	138.0	143.0	137.2	128.9	126.3	...	128.1
1350	125.2	125.3	126.6	127.2	127.8	127.7	126.7	129.4	127.2	132.0	132.0	132.0	132.0	124.1	126.8	132.0	139.0	139.0	144.0	138.4	129.3	126.7	...	128.1
20 (repeat)	13.0	14.2	16.8	17.3	18.5	17.0	16.6	19.6	21.5	25.5	23.6	25.6	31.1	23.6	25.6	42.6	64.7	60.0	82.3	71.8	51.6	55.9	...	56.0

* Steels heated discontinuously; all others heated at steady rate of about 3° C./min.

† Value depends appreciably on time of heating in this temperature region.

‡ Value depends to lesser extent on time of heating in this temperature region.

were drawn to fit the results. Values of the electrical resistivity read from these curves and expressed in microhm centimetre units are given for carbon, alloy, and high-alloy steels in Table XXV. for temperatures of 0° C. (by slight extrapolation), 20° C., 50° C., and thereafter at 50° C.

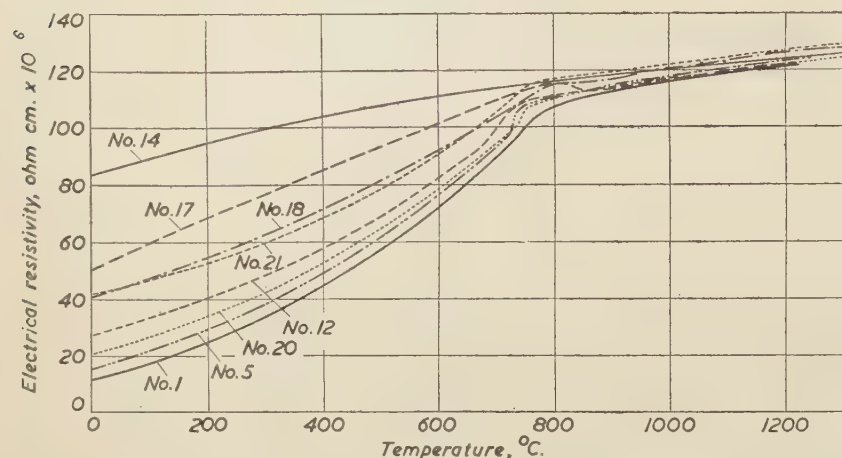


FIG. 14.—Variation of Electrical Resistivity of Steels with Temperature.

intervals to the highest temperature reached. At the lower temperatures the values can be compared with those given previously.¹⁰ Differences are to be noted in some cases, notably for steels 5, 6, 9, 10, 11, 12, 13, 14, 16, and 18, and result from the measurement being made on different samples.

Curves showing the variation of electrical resistivity with temperature of selected steels from each group are reproduced in Fig. 14. The inclusion of all the curves would have caused overcrowding, but those reproduced serve to show the general nature of the variation of resistivity with temperature for the present series of steels.

Points to be noted from the figure are :

(i) The wide range of values embraced by the series at normal temperatures (at 20° C. this extends from 13.0 microhm cm. for steel 1 to 84.2 for steel 14).

(ii) The marked increase in resistivity which occurs with increase of temperature as the transformation region is approached in the case of the carbon and alloy steels, and its absence in the case of the highly alloyed austenitic steels.

(iii) The convergence of the curves towards a relatively narrow range of values beyond the transformation region, and the close similarity in the temperature coefficients of resistance possessed by most of the steels from about 900° C. upwards.

(iv) The curve for steel 17 resembles that obtained for steel 16 in that the resistivity decreases over a short temperature range just above 800° C.

The resistivity curves obtained for the six high-alloy steels during the first tests with discontinuous heating are reproduced in Fig. 15. The decreases in resistivity which occurred with certain steels on prolonged heating can be clearly followed. These changes were most marked with steel 13, and Fig. 16 reproduces the results obtained for this steel from this first method and also those from the

subsequent experiment in which the temperature was steadily increased. The two sets of data are seen to be in agreement up to 340° C., the temperature at which a small decrease had been first noticed in the resistivity during the earlier experiment. Thereafter, the curve obtained when the

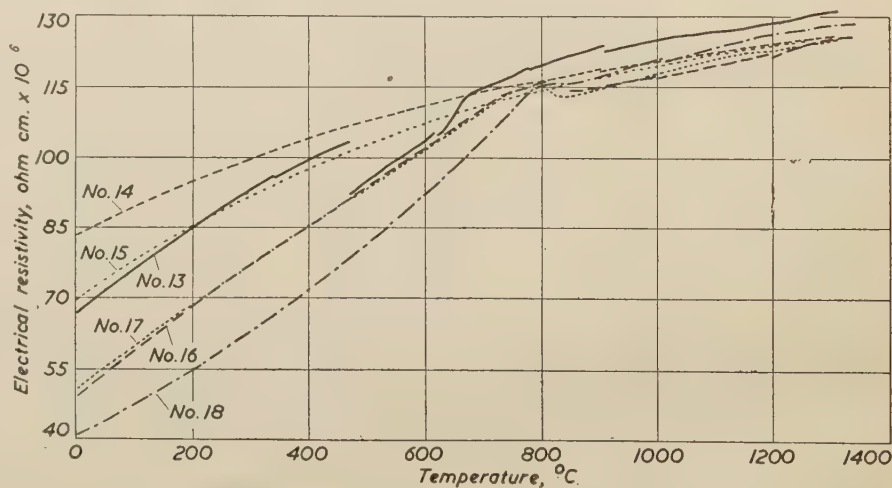


FIG. 15.—Variation of Electrical Resistivity with Temperature for High-Alloy Steels.

specimen was continuously heated lies above that obtained when the heating was discontinuous. The large decrease in resistivity in the region 470° to 670° C. is much less pronounced when the readings are taken with a steadily increasing temperature. There is, however, a distinct depression in the curve in this region. From 680° to 910° C. the two resistivity curves are again in

relatively close agreement. In the test with discontinuous heating it was at this stage that an over-night temperature rise from 903° to 910° C. had been accompanied by a drop of 1.3% in the resistivity curve. There is no evidence of any such change in the second curve, but it will be noticed that it is just at this temperature that the rate of increase of resistance with temperature commences to fall off rapidly.

The main reason for including steel 18 with steel 13 in this repeat test was to obtain additional results at the highest temperatures, since it had been shown previously¹¹ that thermal arrests could occur above 1300° C. Apart from the few check measurements made on this specimen of steel 18 at lower temperatures which are included in Table XXV., the measurements were made from about 1020° C. upwards and these data are also plotted in Fig. 16. It will be seen that the slower rate of rise which previously commenced at about 1200° C. is no longer evident, and that the curve obtained when steel 18 was continuously heated has a marked upward curvature beyond 1310° C.

The experiment could not be conducted beyond 1335° C. owing to the failure of the resistance circuit, and on dismantling the apparatus it was found that the rod of steel 18 had commenced to melt at the temperatures to which it had been subjected (probably about 1350° C.).

The specimen of this steel, whilst still more or less retaining its rod-like form, had fallen to the base of the furnace and had folded up into short sections which had become welded together where they made contact with one another. Two small spheres of metal about 0.1 in. in dia. were also noticed.

It has been shown¹¹ that small areas of liquid can commence to form in this steel at 1315° C. and that these areas increase with increase in temperature. In Fig. 16 the curve of resistivity against temperature is seen to bend upwards at about the temperature at which this formation of liquid commences, but it is not certain whether this change can be attributed to a difference in resistivity accompanying the formation of the liquid phase, or whether it is merely due to the thinning of the rod at the section where fracture eventually occurred. It will be remembered that in this test the accompanying rod was of steel 13 which, having a much greater coefficient of expansion, would

tend to stretch the rod of steel 18. The first rod of this steel to be tested, which neither broke nor showed this sudden increase in resistivity, had been more freely mounted and had had a considerably different type of heating.

Table XXV. also contains values for the resistivity of each steel as measured at the conclusion of the test. In only a few instances do these repeat values agree exactly with the initial values, and occasionally a large increase or decrease in resistivity is seen to have occurred. Such differences can be attributed to several possible causes, for instance, some loss of constituents or a certain amount of oxidation may have taken place at the highest temperatures. The most likely cause, however, is that the final furnace cooling may have differed appreciably in some instances from the procedure originally adopted by the suppliers of

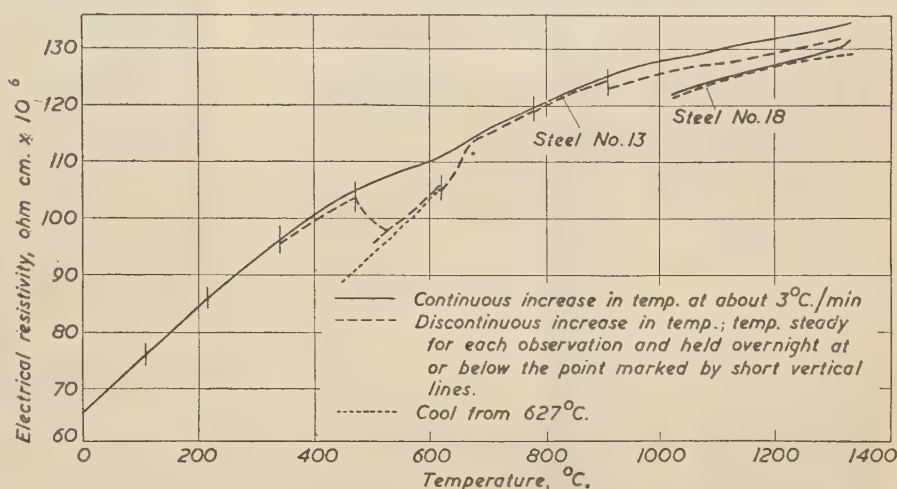


FIG. 16.—Variation of Electrical Resistivity with Temperature for Steels 13 and 18.

the steel. It is fairly certain that this last factor can account for much of the large decrease in resistivity observed in steel 13 and possibly for the increase in resistivity of steel 18.

Another factor affecting the accuracy of the results is that some contamination of the thermocouples may have occurred at high temperatures. This possibility was not examined in detail as it was considered that the accuracy of the present resistivity measurements would more than suffice for the main purpose of the investigation—the estimation of thermal-conductivity values from electrical-resistivity data. The specific-heat determinations carried out subsequently (see Section IB.) confirmed that contamination of Chromel/Alumel thermocouples became serious above 1150° C. Most of the specimens would be above this temperature for about 1 hr. and the observed temperatures may be a few degrees low in consequence. Should contamination have occurred, the high-temperature resistivity values given in

Table XXV. would tend to be too great. However, as the rate of change of resistivity with temperature is small above 1150°C ., an error in temperature measurement of some $50\text{--}60^{\circ}\text{C}$. would be required to cause an error of 1% in the electrical resistivity. It is very unlikely that the thermocouples are affected to this extent, so the present electrical-resistivity values are probably correct to within 1% at all temperatures. This conclusion has received independent support, since measurements made in the course of the specific-heat determinations described in Section IB. also provide data for the evaluation of the

point from the true curve of resistivity against temperature. This method of plotting discloses abrupt changes of slope and usually sharp peaks

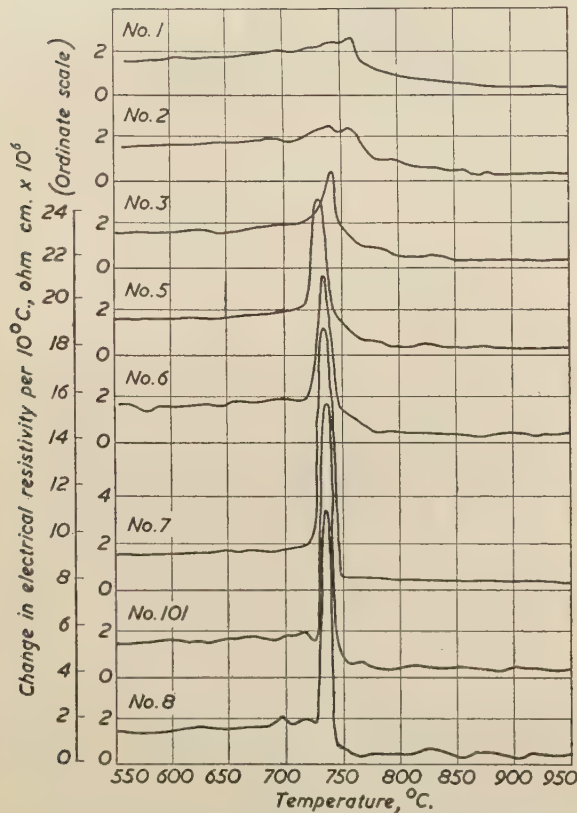


FIG. 17.—Change in Electrical Resistivity per 10°C . against Temperature for Carbon Steels.

electrical resistivity of each steel. In general, the two sets of values agree to within 1%; the values differ by as much as 2% for steels 3 and 7 only, those given in Table XXV. being the lower.

In order to be able to appreciate more readily the extent to which variations in the rate of change of resistance with temperature correspond with changes noted in other properties of the steels, increments of resistivity for every 10°C . have been read off from the large-scale graphs and plotted in Figs. 17–20 against the mean temperature for the interval. As repeat measurements have not been made, some of the small kinks in these curves may reflect the departure of an experimental

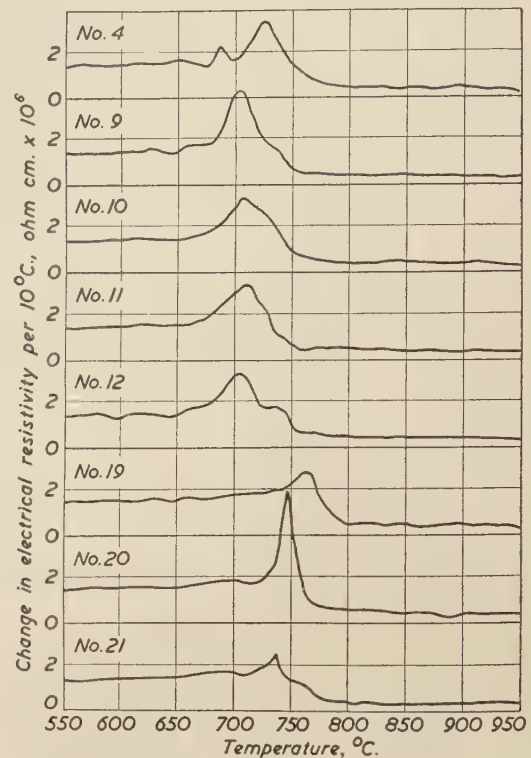


FIG. 18.—Change in Electrical Resistivity per 10°C . against Temperature for Alloy Steels.

TABLE XXVI.—Temperatures of Main Peaks in Curves Showing Change of Resistivity with Temperature.

Steel.	Temp. of Main Peaks, $^{\circ}\text{C}$.	
1	735	758
2	735	755
3	737	
5	726	
6	732	
7	732	
101	734	
8	733	
4	686	725
9	702	
10	705	
11	710	
12	702	
19	760	
20	745	
21	736	
13	650 *	664 †
16	810 approx.	
17	805	
18	830	

* Discontinuous heating. † Heated at $3^{\circ}\text{C}/\text{min}$.

occur in the curves for those steels which undergo phase transformations. From Fig. 17, which relates to the carbon steels, it will be seen that steels 1 and 2 give two small peaks, the remaining carbon steels having one clearly defined main peak, the height of which increases with increase in carbon content to reach a maximum value for the steel of the eutectoid composition. The peak occurs at a lower temperature for steel 5 and this holds also for the specific-heat curves (see Figs. 156A and 156B of the previous report¹²). From the curves in Fig. 18 for the alloy steels it is seen that in general the peaks are broader and lower. Of the three high-alloy steels treated in Fig. 19, the curves for steels 14 and 15 are relatively featureless, but those for steel 13 reflect the changes which occur when the steel is maintained at temperatures of 300–680° C., the effects being more pronounced for the case shown as a full line where the steel was kept at these temperatures for the longer time. Fig. 20 relates to the remaining steels, 16, 17, and 18, which are similar in that the main peak is negative.

The temperatures corresponding to the main peaks for each steel are set out in Table XXVI. As with the interpretation of the somewhat similar specific-heat curves, some doubt exists as to whether the incidence of a phase transformation is

associated with the initial change of slope rather than with the peak itself.

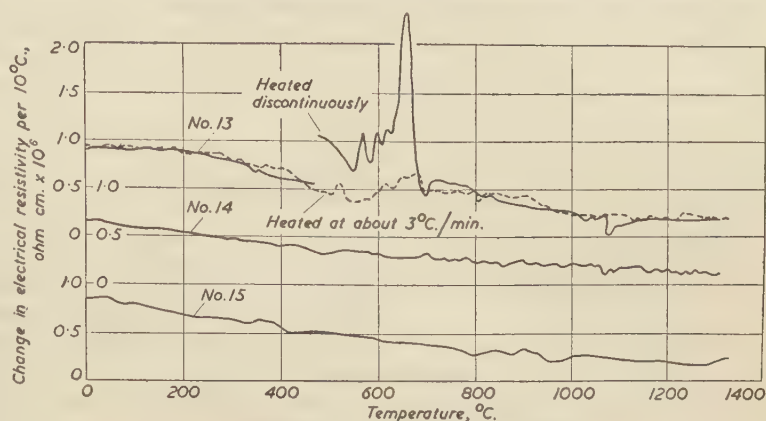


FIG. 19.—Change in Electrical Resistivity per 10° C. against Temperature for Steels 13, 14, and 15.

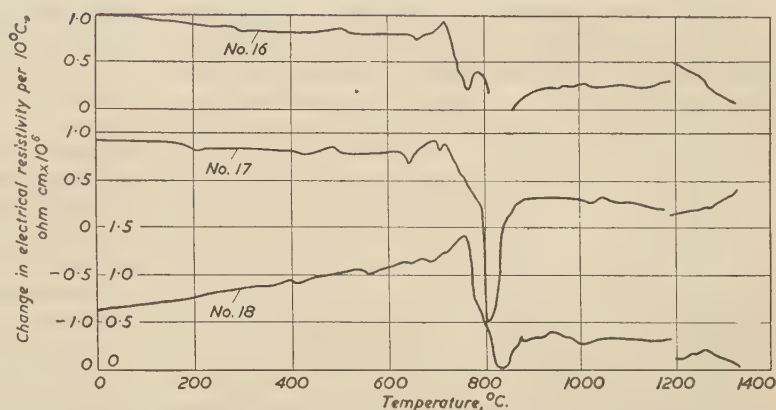


FIG. 20.—Change in Electrical Resistivity per 10° C. against Temperature for Steels 16, 17, and 18.

Section III B.—Effect of Heat-Treatment on the Electrical Resistivity and Thermal Conductivity of a 13% Manganese Steel (Steel 13); Thermal-Conductivity Values up to 850° C.

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(Fig. 28 = Plate IX.)

INTRODUCTION.

Steel 13, which forms the subject of the present section, was stated to contain elements additional to iron in the following amounts :

Carbon, %	1.22
Silicon, %	0.22
Manganese, %	13.00
Sulphur, %	0.01
Phosphorus, %	0.038
Chromium, %	0.03
Nickel, %	0.07
Copper, %	0.07

Aluminium, %	0.004
Arsenic, %	0.038

The specimens had been heated to 1050° C. and cooled in air.

In the report previously published¹³ this steel was mentioned as the only one in which the temperature involved in the conductivity tests to 350° C. had had any appreciable influence on the conductivity of the steel. The electrical-resistivity determinations described in the foregoing section confirmed the occurrence of marked changes when steel 13 was maintained at tempera-

tures within the approximate range 300–700° C. The present Section contains the results of experiments made with a view to studying these changes in greater detail and of determining their effect

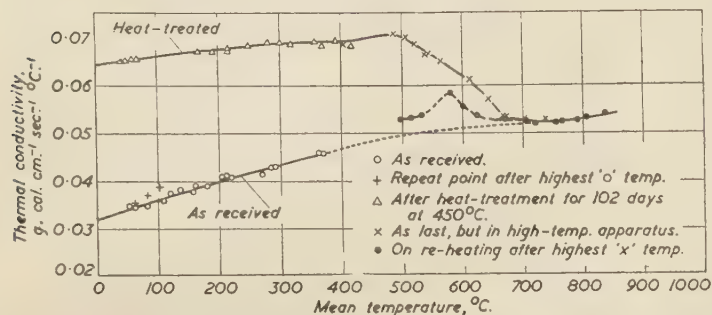


FIG. 21.—Variation of the Thermal Conductivity of Steel 13 with Temperature and Heat-Treatment.

on both electrical resistivity and thermal conductivity.

Electrical resistivity is shown to be a property which can readily be used to follow the effect of heat-treatment on the steel. X-ray photographs

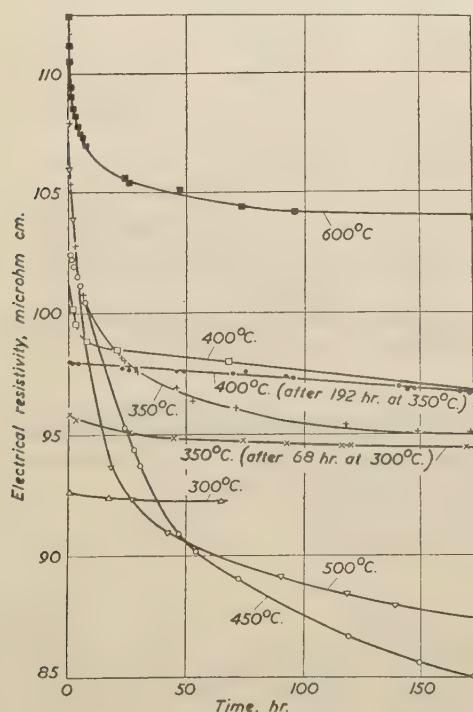


FIG. 22.—Effect of Heat-Treatment at Various Temperatures on the Electrical Resistivity of Steel 13.

which have assisted in interpreting the nature of the structural changes are included.

This Section also contains results for the thermal conductivity and electrical resistivity up to 850° C. of steel 13 in the as-received condition and after being heat-treated at 450° C. for 102 days.

INFLUENCE OF HEAT-TREATMENT ON THE ELECTRICAL RESISTIVITY.

The small changes in thermal conductivity produced by the heat-treatment involved in the above-mentioned determination to a mean temperature of 350° C. can be seen from Fig. 21 of the present work. The lower curve reproduces the results of this earlier work, and the three repeat points (marked as +) are seen to depart from this curve. The extent of the departure is greatest for the section of the specimen which has been heated to the highest temperature, and it was concluded that the change commenced when the steel was heated above about 300° C.

To investigate the matter further, electrical-resistivity measurements have been made on small rods, about 10 cm. in length and 0.5 cm. in dia., maintained at uniform temperatures for noted periods of time. The results of these tests are shown in Figs. 22–25. Each specimen was mounted in a closed-ended refractory tube which could be evacuated throughout the test and was heated by being inserted into a wire-wound tubular furnace. Thermocouples and potential leads were welded to the specimen and the resistivity determination carried out in the normal way. In view of the number of tests made, it is convenient to letter each specimen and to consider each one separately.

Specimen A.—This specimen was maintained at 300° C. for nearly 3 days, during which time the resistivity decreased from 92.6 to 92.2 microhm cm. The temperature was then raised to 350° C. and kept at this value for 8 days. During this period the resistivity of the steel again decreased, this time from 95.8 to 94.4 microhm cm.

It will be seen from Fig. 22 that the curves for the change of resistivity with time at 300° and 350° C. are of the same type and that perfectly constant values had not been reached. Both yielded straight lines when the resistivity and time were plotted logarithmically, as in Fig. 25, and it was considered that longer heat-treatment would have little further effect at these temperatures.

The temperature of the specimen was then increased to 400° C. The initial rate of decrease in resistivity proved to be less than at 350° C., but instead of being exponential the decrease was now approximately linear for about the first 45 days. At this stage the resistivity had changed from 98.0 to 89.8 microhm cm. The rate of decrease in resistivity then became less and the curve became approximately exponential, as is shown by the relatively straight line now obtained on the logarithmic plot in Fig. 25. After 195 days, when the resistivity had fallen to 79.8

microhm cm., the specimen was removed from the furnace and air-cooled.

The electrical resistivity at 20° C. was measured and found to be only 47.5 compared with an initial value of 68.5 microhm cm.

These results can be followed by reference to Fig. 24. The upper continuous line is reproduced from Fig. 16 and shows the variation with temperature of the resistivity of an as-received specimen of the steel when heated to 1330° C. at the rate of 3° C./min. The heavy vertical lines show the extent of the resistivity changes which occurred when the steel was maintained at steady temperature. The foregoing history of the present sample can be traced by following the appropriate interconnecting dotted lines. The resistivity value reached after 195 days at 400° C. is joined to the subsequent value obtained at room temperature by a straight line shown as a series of dashes. It is not to be assumed that this line or other similar lines give the actual resistivity curve on cooling, as intermediate points were not obtained.

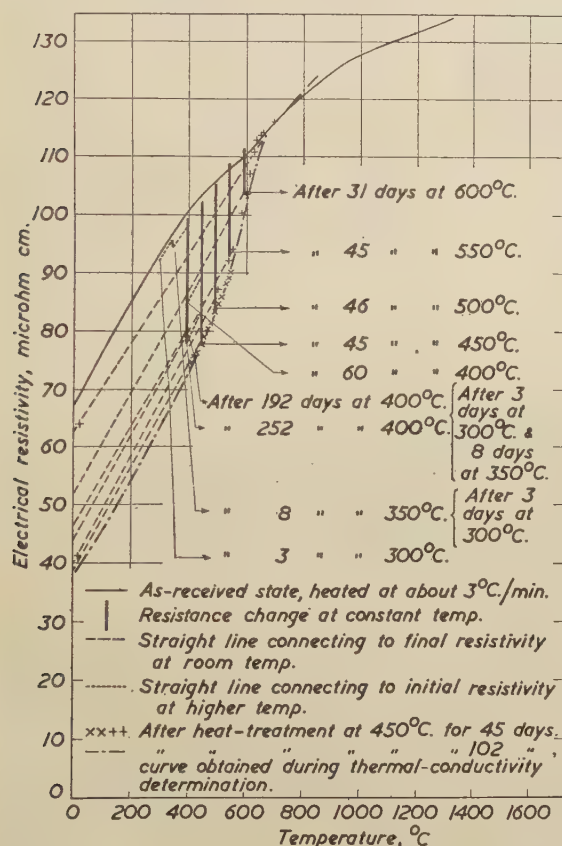


FIG. 24.—Dependence of Electrical Resistivity on Temperature and Heat-Treatment of Steel 13.

After an X-ray photograph of the specimen had been recorded the rod was joined to a new rod of

the steel (specimen *B*), again sheathed in the evacuated refractory tube, and returned to the 400° C. furnace. The experiment was continued

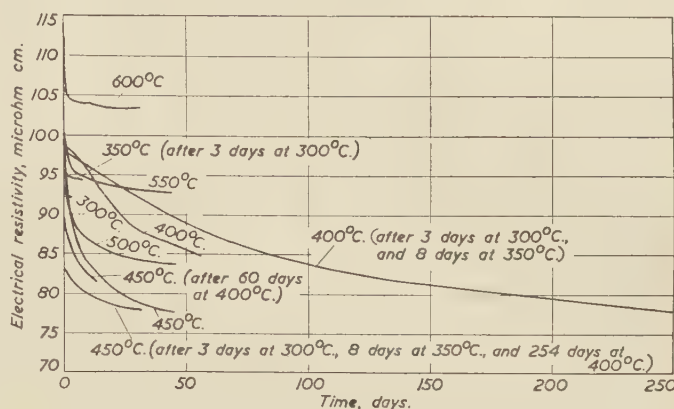


FIG. 23.—Effect of Prolonged Heat-Treatment at Various Temperatures on the Electrical Resistivity of Steel 13.

for a further 60 days at 400° C., by which time the resistivity of specimen *A* (at 400° C.) had decreased to 77.7 microhm cm. The temperature was then increased to 450° C. The first resistivity measurement made at this new temperature was 83.0. The subsequent more rapid decrease in resistivity can be followed from Fig. 23. After 32 days at 450° C. the resistivity was 78.0 microhm cm. and was still decreasing.

Specimen B.—This specimen had the same thermal history as that described for specimen *A* in the last paragraph of the foregoing section. It differed from *A* in that the resistivity changes observed at 400° C. were obtained for a steel rapidly heated to that temperature, whereas *A* had already undergone changes at 300° and 350° C. The initial resistivity-time curve (Figs. 22 and 23) is now quite different. The resistivity decreases rapidly for the first 8 hr. or so, and then more slowly. After 8 days the rate of decrease increases and is much more rapid than that of specimen *A* at the same resistivity. It would appear that the changes accompanying the heat-treatment of specimen *A* at 300° and 350° C. have an inhibiting effect on the changes at 400° C.

The logarithmic plots of both experiments at 400° C. are approximately linear in their initial stages and only curve downwards after about 8 days. This result raises the question whether something similar would have occurred at 350° C. and possibly at 300° C. had these experiments been extended to longer times. Such experiments have not yet been carried out.

Specimen C.—This specimen was introduced into a furnace maintained at a temperature of 450° C. The resistivity fell linearly from 102.5 to 95.2 microhm cm. during the first 24 hr., after which the rate of decrease tended to become exponential, and a resistivity value of 77.6 was

reached after 45 days. As will be seen from Fig. 23, this specimen reached resistivity values after about 3 and 12 days respectively which were given at 450° C. by specimens *B* and *A* after their much longer heat-treatments at lower temperatures. There again appears to be evidence for some inhibiting effect introduced by the heat-treatment at the lower temperatures.

After 45 days at 450° C. the specimen was quickly cooled to room temperature, when the resistivity at 20° C. was only 39.7 microhm cm., and an X-ray photograph was obtained.

It was then decided to heat the specimen to the higher temperature of 550° C. to see whether carbides revealed by the X-ray photographs went back into solution. The heating from 420° C. to 554° C. occupied about 2 hr., during which the resistivity-temperature course shown by \times in

had been 57% less than the original. On finally heating this specimen to a bright red heat by means of a blow pipe and either air-cooling or quenching in water, room-temperature resistivities agreeing to within 1% with the original value were obtained.

Specimen D.—This specimen was maintained for 46 days at a temperature of 500° C., during which time the resistivity fell approximately exponentially from 106.0 to 83.8 microhm cm. The effect of the heat-treatment is seen to be a little less pronounced than that at 450° C. The final resistivity on cooling to 20° C. was 40.7, compared with the value of 39.7 microhm cm. after specimen *C* had been heated for a similar time at 450° C. An X-ray photograph showed less carbide to be present.

Specimen E.—This specimen was maintained for 45 days at 550° C., during which time the resistivity fell exponentially at first, but thereafter at a slower rate from 109.0 to 93.0 microhm cm. This heat-treatment was again less effective, and the final resistivity at 20° C. was higher, namely, 44.9 microhm cm.

Specimen F.—This specimen was maintained for 31 days at 600° C., and the resistivity decreased from 111.5 to 103.5 microhm cm. Again the change was exponential at first and then appeared to become more constant. This latter stage was masked to some extent by small fluctuations in the furnace temperature. The initial resistivity at 600° C. for this specimen, and

also that for specimen *E* at 550° C., was 1 or 2% above the original resistivity-temperature curve given in Fig. 24. This resulted from these specimens being heated five or six times as rapidly and having less opportunity for changes to occur once the range 300–600° C. had been entered. On cooling, the resistivity of specimen *F* at 20° C. was 53.0 microhm cm.

Specimen G.—This specimen was the rod of 1-in. dia. steel which had already been used for the determination of the thermal conductivity of steel 13 in the as-received condition up to 350° C. The specimen was enclosed in an evacuated refractory tube and maintained at a temperature of approximately 450° C. for a period of 102 days. This was done with a view to determining at a later date the thermal conductivity of the heat-treated steel. No resistivity measurements were made during the heat-treatment, but the final value at 20° C. was observed and found to be 38.8 microhm cm. This value is included for

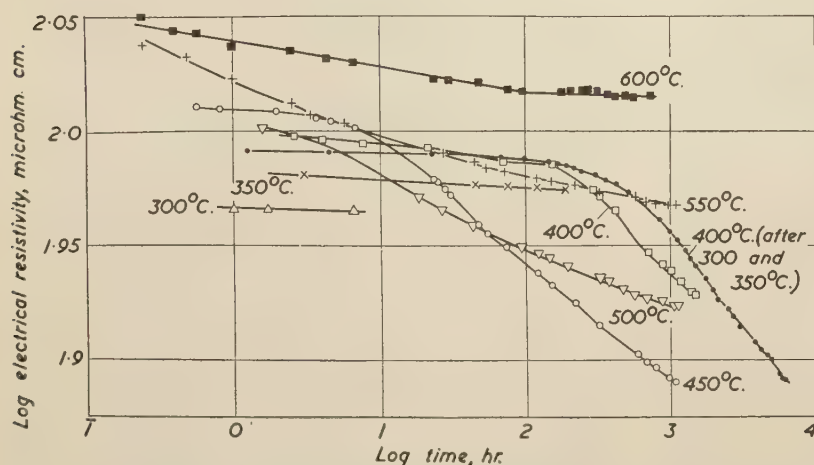


FIG. 25.—Logarithmic Plot of Electrical Resistivity against Time of Heating at Various Temperatures for Steel 13.

Fig. 24 was followed. The specimen was then removed from the furnace and cooled. The electrical resistivity at 20° C. had now increased to 40.7 microhm cm., but the X-ray photograph remained similar to that previously obtained, *i.e.*, the carbides had not gone back into solution. The full results of the X-ray analysis will be discussed later.

It was next decided to heat the specimen to higher temperatures to ascertain whether the present resistivity-temperature curve joined into that previously obtained for the steel when tested in the as-received condition. The points so obtained are shown in Fig. 24, marked $+$, and it will be noted that these points join the original curve at about 650° C. and follow it reasonably well to higher temperatures. On again cooling and measuring at 20° C. the resistivity was found to have increased to 63.7 microhm cm., that is, to within 7% of its original value, whereas the lowest value reached after the heat-treatment at 450° C.

completeness in Fig. 24, as is also the curve of resistivity against temperature obtained subsequently in the course of the thermal-conductivity determinations described later in this report.

It would seem that the resistivity of steel 13 after being heated to a temperature in the range 300–700° C. can lie anywhere in the space between this last-mentioned curve for an extensively heat-treated steel and that first given for the as-received condition, and it may be even lower after more prolonged heating at about 450° C. The value will depend on the thermal history of the sample.

DESCRIPTION OF THERMAL-CONDUCTIVITY AND ELECTRICAL-RESISTIVITY MEASUREMENTS ON STEEL 13, AFTER HEAT-TREATING AT 450° C. FOR 102 DAYS (SPECIMEN G).

The longitudinal heat-flow method previously described⁸ was first used for determination of the thermal conductivity and electrical resistivity of steel 13 in the above heat-treated condition (specimen G) up to a mean temperature of about 400° C. The results obtained for the thermal conductivity are plotted in the upper section of Fig. 21 and those for the electrical resistivity in the lower section of Fig. 26. The results pre-

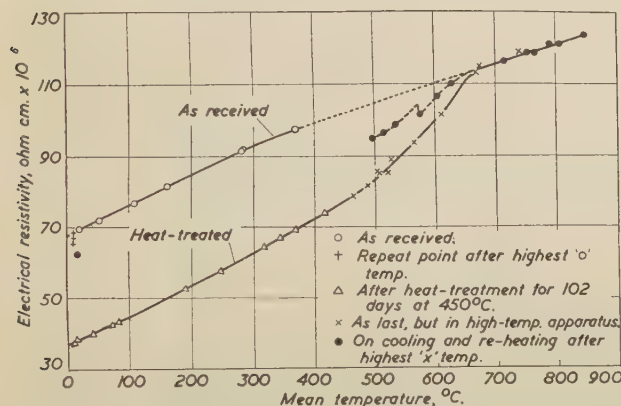


FIG. 26.—Variation of Electrical Resistivity of Steel 13 with Temperature and Heat-Treatment.

viously reported for the as-received state are included in these figures. It will be seen (Fig. 21) that the heat-treatment has caused the thermal conductivity when extrapolated to 0° C. to increase from 0.031₅ to 0.064 g. cal. cm.⁻¹ sec.⁻¹ C.⁻¹, that is, to become approximately doubled. At 360° C. the corresponding increase is from 0.045 to 0.069. The accompanying changes in the electrical conductivity, the reciprocal of the resistivity, are a little smaller.

A somewhat similar longitudinal heat-flow method, which is described in detail in Section IIIc., was used to extend the measurements to higher temperatures. The results are shown

(marked ×) in Figs. 21 and 26 and will be seen to agree at about 400° C. with those of the low-temperature assembly. The thermal conductivity continues to increase slowly up to a value of about 0.070 at 500° C. In this region a steady decrease is observed to occur which continues until a value of 0.053 is reached at 670° C. Values of this order were obtained up to a temperature of 740° C. at which stage the specimen was cooled to room temperature. The electrical resistivity at 20° C. was then 62.5 microhm cm., indicating that much of the effect of the original heat-treatment had been destroyed. Repeat values for the thermal conductivity obtained in the range 500–630° C. were now lower than those originally determined, but conditions were not steady as there was a noticeable tendency for the conductivity, both thermal and electrical, to increase with time of heating within this range of temperature.

Good agreement was however obtained with the earlier values over the range 690–740° C., and the determination was extended to a maximum temperature of 840° C. At these higher temperatures the thermal conductivity of the steel is again seen to have a small positive temperature coefficient. In fact, these results can be regarded as lying on a fair continuation of the curve obtained at lower temperatures for the steel in the as-received condition, and in Figs. 21 and 26 the intervening portions of the curves are shown as a series of dots. The electrical-resistivity curve obtained in this way (Fig. 26) commences from a level at 400° C. about 1.5% below the uppermost curve of Fig. 24, that for the steel when heated from the as-received state at a fast rate, and conforms more closely with it from 500° C. onwards. It is reasonable to assume that the corresponding dotted curve shown in Fig. 21 represents, to within similar limits of accuracy, the thermal conductivity of the steel when rapidly heated from the as-received state. As has already been shown for the electrical resistivity of steel 13, similarly, the thermal conductivity is not reproducible above about 300° C., but may assume values lying between the two main curves shown in Fig. 21, or may even assume slightly higher values after being heated for a longer period in the region of 450° C.

Values of the thermal conductivity and of the electrical resistivity read off at 50° C. intervals from the curves for the as-received and heat-treated conditions are set out in Table XXVII. This Table also contains values for the Lorenz function, the product of the thermal conductivity and electrical resistivity divided by the absolute temperature. Curves showing the variation of the Lorenz function with temperature are given in Fig. 27, and the theoretical value of 0.586×10^{-8} , predicted by Sommerfeld on the assumption

TABLE XXVII.—*Thermal Conductivity, K (g.-cal. cm.⁻¹ sec.⁻¹ °C.⁻¹), Electrical Resistivity, ρ (ohm cm.), and Lorenz Function, $K\rho/^\circ\text{Abs.}$, of Steel 13 in the As-Received Condition and after being Heat-Treated at 450° C. for 102 Days.*

(Values are uncorrected for dimensional changes of specimen with temperature.)

Temperature.		Condition of Steel 13.					
° C.	° Abs.	As Received.			Heat-Treated.		
		Thermal Conductivity.	Electrical Resistivity, $\times 10^6$.	Lorenz Function, $\times 10^8$.	Thermal Conductivity.	Electrical Resistivity, $\times 10^6$.	Lorenz Function, $\times 10^8$.
0	273	0.031 ₅ *	67.0 *	0.77 ₅ *	0.064 *	37.4 *	0.88 *
50	323	0.033 ₅	71.5	0.74 ₅	0.065	40.7	0.82
100	373	0.035 ₅	75.8	0.72 ₅	0.066	44.8	0.79
150	423	0.037 ₅	80.2	0.71	0.066 ₅	48.8	0.77
200	473	0.039 ₅	84.5	0.70 ₅	0.067 ₅	53.2	0.76
250	523	0.041 ₅	88.5	0.70	0.068 ₅	57.7	0.75 ₅
300	573	0.043	92.6	0.69 ₅	0.069	62.5	0.75
350	623	0.044 ₅	96.0	0.69	0.069	66.8	0.74
400	673	0.046 ₅ *	98.8 *	0.68 *	0.069 ₅	72.1	0.74 ₅
450	723	0.048 *	101.7 *	0.67 ₅ *	0.070	77.0	0.74 ₅
500	773	0.049 *	104.5 *	0.66 ₅ *	0.070	83.1	0.75
550	823	0.050 *	107.2 *	0.65 ₅ *	0.066	90.8	0.73
600	873	0.050 ₅ *	110.0 *	0.64 *	0.061 ₅	99.3	0.70
650	923	0.051 *	112.7 *	0.62 ₅ *	0.055 ₅	110.1	0.66 ₅
700	973	0.051 ₅ *	115.3	0.61 ₅ *	0.052 ₅	115.3	0.62
750	1023	0.052	118.0	0.60	0.052	118.0	0.60
800	1073	0.053	121.1	0.59 ₅	0.053	121.1	0.59 ₅
850	1123	0.053 ₅ *	124.0 *	0.59 *	0.053 ₅ *	124.0 *	0.59 *

* Extrapolated value.

that both thermal and electrical conduction are the result of electronic agencies, is also indicated. The results for the present steel resemble those already obtained for ingot iron ¹⁴ and for steel 7 (see Section IIIc.) in that the Lorenz function tends

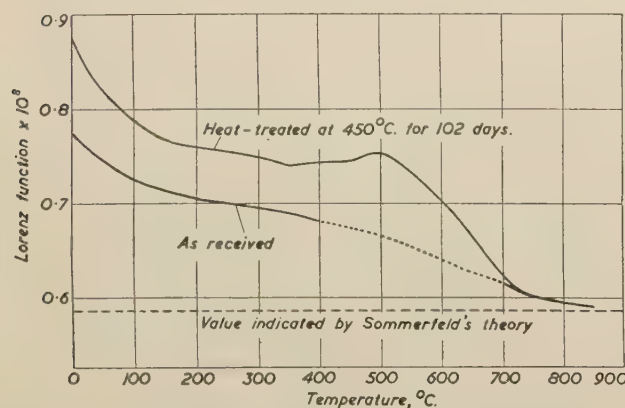


FIG. 27.—Variation of Lorenz Function of Steel 13 with Temperature and Heat-Treatment.

to approach the electronic value at high temperatures, but is much greater at lower temperatures.

Another interesting fact, and one which is important when a knowledge of the Lorenz function is assumed to estimate thermal-conductivity values from electrical-resistivity data, is that the Lorenz function has different values for the two conditions in which steel 13 has been tested. The

curve for the heat-treated condition lies above that for the as-received condition, the difference amounting to about 13% at room temperature. An error of this order would have been introduced, had the value of the Lorenz function for the as-received condition been used to predict the thermal conductivity of specimen *G* from the data first obtained for its electrical resistivity. The predicted value would have been too low.

It is usually thought that a high Lorenz function can be explained by the contribution made by the crystal lattice to the thermal conduction, but not to the electrical conduction. The heat-treatment has, in the present instance, brought about changes in the steel which have led to its electrical conductivity being increased. Had the proportion of the thermal conductivity which is attributed to non-electronic factors remained unaltered by the heat-treatment, a decrease in the value of the Lorenz function would have been anticipated. It is clear that this is not the case, and that either the non-electronic conduction factor has been increased in much greater proportion by the heat-treatment, or some additional factors have to be considered in connection with the conductivities of steels. Fig. 37 (in Section III d.) suggests that the latter is the case and indicates that at a particular temperature the Lorenz function of a steel in the α -phase is greater than when in the γ -phase. It is possible that there are complications due to the restrictions which magnetism imposes on the

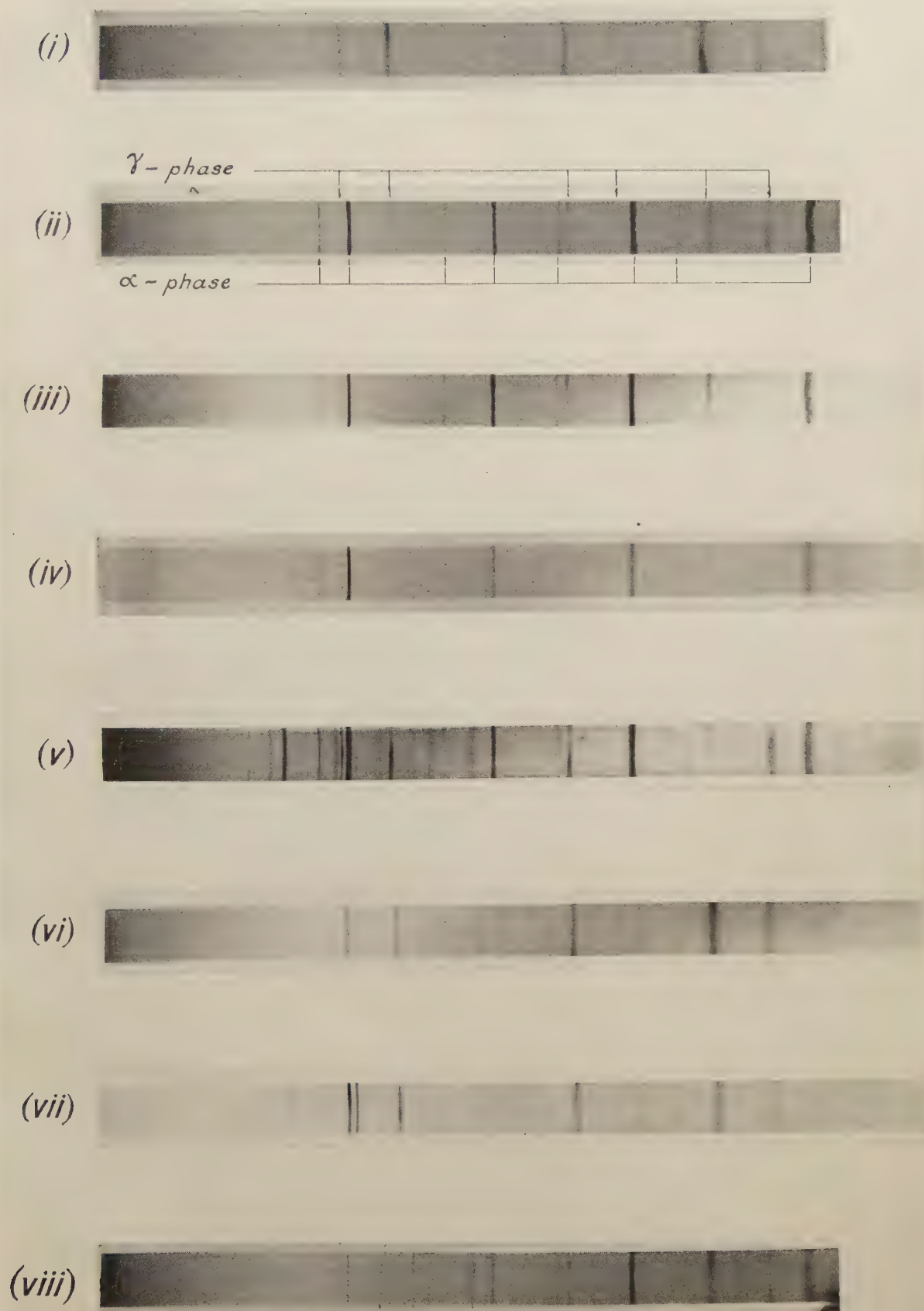


FIG. 28.—X-Ray Photographs of Steel 13.

[National Physical Laboratory.
[To face p. 110 P.]

freedom of the electrons. Steel 13 was not noticeably magnetic in its as-received state, but the heat-treated material was quite strongly magnetic. Furthermore, it is above the magnetic-transformation point that the decrease in the Lorenz functions commences for the ingot iron and the steel (7) to which reference has already been made. Moreover, the following X-ray analysis confirms that transformation from the γ - to the α -phase occurred as a result of the heat-treatment.

X-RAY PHOTOGRAPHS OF STEEL 13 IN VARIOUS CONDITIONS.

As stated earlier, X-ray photographs were taken of some of the specimens at various stages in the investigation of the effect of heat-treatment on the electrical resistivity of steel 13. Certain of these photographs are reproduced in Fig. 28 and these will now be described, together with the conclusions reached regarding the structure of the steel.

(i) *Steel 13 in the As-Received Condition.*—This photograph shows the presence of the γ -phase only. Other constituents, such as carbides, are in solution and do not exist in the steel as a separate crystalline entity.

(ii) *Specimen F after 31 Days at 600° C.*—This photograph shows that a high proportion of the steel has been precipitated in the form of the α -phase. There are still spectrum lines present due to the original γ -phase, but it will be noted that there are no lines of appreciable intensity due to constituents other than these two main phases.

(iii) *Specimen E after 45 Days at 550° C.*—This photograph is very similar to (ii), but there are additional faint lines present which indicate the partial formation of material additional to the α - and γ -phases. There are also indications of grain growth.

(iv) *Specimen D after 46 Days at 500° C.*—This photograph again shows the presence of strong α -phase lines with a small amount of the γ -phase. The additional lines are stronger than in (iii).

(v) *Specimen C after 45 Days at 450° C.*—This photograph again shows both α - and γ -phases. In addition, however, there is a striking appearance of many strong additional lines. Some of the lines are due to oxides, but after allowing for these, the remainder indicate the formation of particularly well-crystallized aggregates of additional constituents which are presumably iron-manganese carbides. There is no evidence of any appreciable ϵ -phase.

(vi) *Specimen H (an Additional Specimen) after 1 Day at 400° C.*—This photograph shows the presence of both α - and γ -phases.

(vii) *Specimen H after 8 Days at 400° C.*—This

photograph again shows the α - and γ -phases together with the additional "carbide" lines. The intensity of the latter, however, has diminished considerably. The marked precipitation of the carbides in the region of 450° C. does not characterize this condition at 400° C., despite the relative proximity of the two temperatures.

(viii) *Specimen A after 3 Days at 300° C., 8 Days at 350° C., and 195 Days at 400° C.*—This photograph, compared with (vii), shows that the prolonged heat-treatment at 400° C. has increased the proportion of the α -phase relative to the γ -phase, but has not produced any appreciable further precipitation of "carbides." The amount of carbide produced therefore depends in a sensitive manner on the temperature of heat-treatment, being a maximum in the region of 450° C.

Another photograph, not reproduced, from sample C when finally heated to 550° C. for about 1 hr., showed no noticeable difference from (v).

DISCUSSION OF FOREGOING RESULTS.

It is clear from the above results of X-ray analysis that steel 13, as supplied, contained iron in the γ -phase only and had the additional elements in solution. Heat-treatment at temperatures from 400° to 600° C., inclusive, resulted in much of the iron being transformed to the α -phase. Heat-treatment at temperatures of 400° and 550° C. produced, in addition, some faint lines due to the precipitation of some constituent, and heat-treatment in the region of 450° C. caused these additional lines to appear very strongly. It is suggested that the precipitate constituent consists of carbides of iron or manganese.

No doubt the observed changes in electrical resistivity, which were also most marked at 450° C., can be attributed to these structural changes having taken place in the steel. It seems not unlikely that further work along these lines might enable the alterations observed in the form of certain of the resistivity-time curves to be correlated with the incidence of new lines in the X-ray photograph.

The work carried out to date has shown the value of the electrical-resistivity measurements as a practical method of following the effect of temperature and time of heating on the steel whilst the heating is in progress.

ACKNOWLEDGMENT.

The author wishes to acknowledge that the X-ray photographs and the conclusions derived from them regarding the structural changes were supplied by Dr. W. A. Wood, who was then working in the Physics Division.

Section IIIc.—Thermal Conductivity of a 0.8% Carbon Steel (Steel 7).

By R. W. POWELL, D.Sc., F.INST.P., ASSISTED BY M. J. HICKMAN.

INTRODUCTION.

The present section describes two methods which have been used for the determination of thermal conductivities up to about 1000° C., and contains the results obtained by each method for steel 7, a steel containing the following elements in addition to iron:

Carbon, %	0.80
Silicon, %	0.13
Manganese, %	0.32
Sulphur, %	0.009
Phosphorus, %	0.008
Chromium, %	0.11
Nickel, %	0.13
Molybdenum, %	<0.01
Copper, %	0.070
Aluminium, %	0.004
Arsenic, %	0.021

THE LONGITUDINAL HEAT-FLOW METHOD.

The first method employed was a development of that described in connection with the earlier work which involved the establishment of a longitudinal flow of heat through a bar of the test metal and an extension bar of a metal of known thermal conductivity. The method differed in that the test-bar was now uppermost and was heated at its upper end, the base was no longer water-cooled directly, and the whole apparatus was surrounded by a gas-tight cover so that it could be evacuated to prevent excessive oxidation of the specimen at high temperatures. The general arrangement of the apparatus is shown in Fig. 29. The specimen used was the same bar as that on which the earlier measurements were made.⁸ A heating coil composed of platinum wire wound on a steatite former was inserted in a hole at one end of the bar. On the other end a 7° taper was machined over a length of 1 in. to enable the bar to be securely joined to the standard bar. The latter was supported vertically on a steel base-plate. Thermocouples composed of fine platinum/platinum-rhodium alloy wires were pegged into the two bars and these were surrounded by a steel furnace tube also provided with thermocouples and having heating units at the top, centre, and base. The uppermost furnace heater was composed of platinum wire supported by a steatite former and the others were of Nichrome wound on mica insulation. Stout metal wires were firmly attached to the top and bottom of the composite bar to serve as current leads for the measurement of the electrical resistivity of the test-specimen. All leads and thermocouples were brought out through four steel tubes welded to the steel base-

plate and gas-tight joints were made by means of wax seals. The interspace between the furnace tube and the specimen was packed with heat-insulating powder, and similar insulation retained between a larger steel tube and the furnace prevented excessive loss of heat from the latter. The whole apparatus was enclosed by a thick-

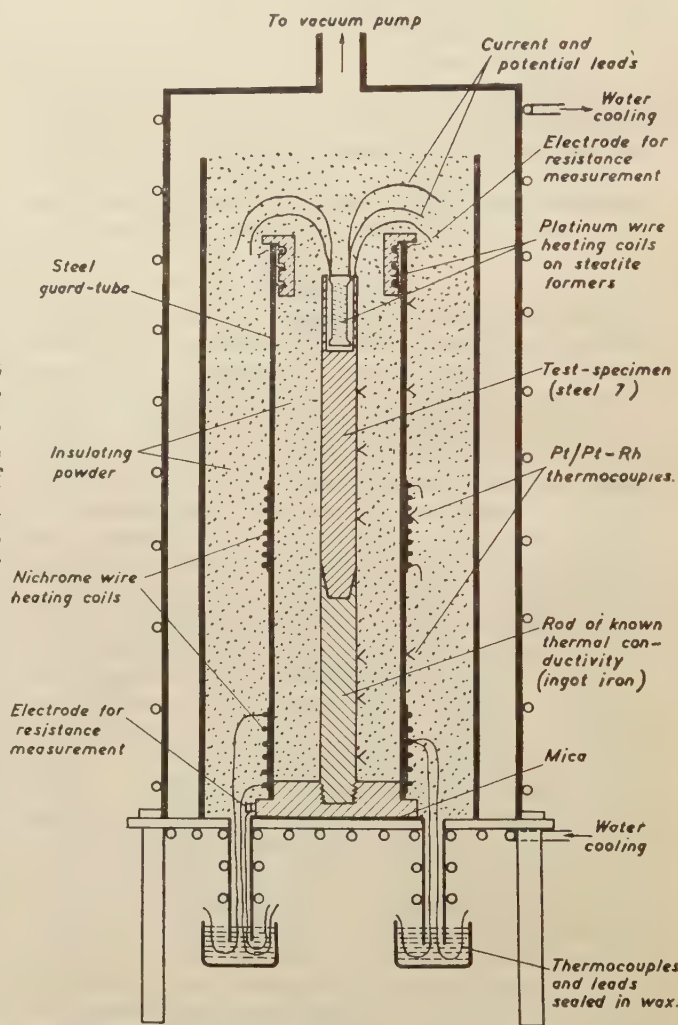


FIG. 29.—Apparatus for Determination of Thermal Conductivity by Longitudinal Heat-Flow Method.

walled, water-cooled steel cover which could be sealed to the steel base-plate and evacuated through a tube welded in the top. Tubes for cooling water were also soldered to the base-plate and to the four tubes leading to the wax pots.

The experimental method was the same as that used previously at lower temperatures, the energy flowing in the test-bar being derived from the

temperature gradient established in the bar of known thermal conductivity, a correction being

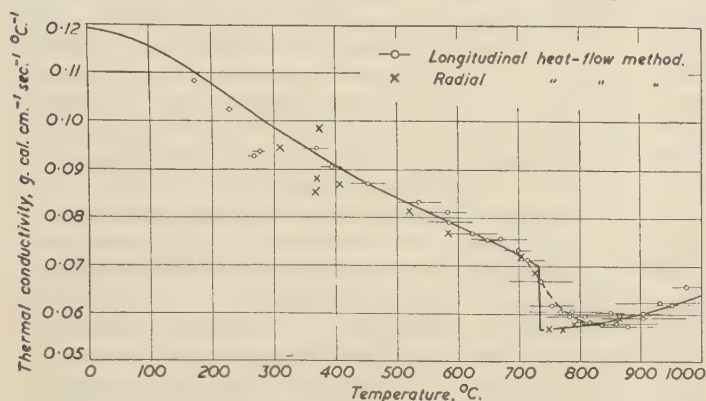


FIG. 30.—Variation of Thermal Conductivity of Steel 7 with Temperature.

applied to allow for any lateral heat transfer which occurred when exactly matched conditions of furnace and specimen were not attained.

Measurements of electrical resistivity were made from time to time using the thermocouples attached to the bar as potential leads.

RESULTS BY LONGITUDINAL HEAT-FLOW METHOD.

The experimental results obtained for the thermal conductivity of steel 7 by the method described above are shown in Fig. 30. The small circles denote the mean temperature to which the value corresponds, and the horizontal lines drawn through these circles extend to the actual temperatures used in making the determination. Over the range 0–300° C. the smooth curve drawn in Fig. 30 is based on the previous results for this steel, and at higher temperatures it passes through the mean of the new experimental values. At the lower-temperature end, where the energy flowing in the bars is small, there is seen to be a fair amount of scatter in the experimental points. This results from the smaller differences between the thermocouple readings and from the relatively greater effect of any lateral interchange of heat occurring between the points at which the two gradients are measured. These errors decrease in importance at higher temperatures where larger heat flows were generally employed. Provided that the thermal conductivity remained constant, or varied linearly with temperature, it would therefore be advantageous to establish a relatively large heat flow in the bars. Care must be taken, however, to ensure that the use of large temperature differences does not mask any departures from constancy or uniform variation of thermal conductivity. In the present instance there are strong indications that such a change occurs above 700° C., that is, in the transformation region of the steel, and it became apparent that this method

was not well suited to the determination of the detailed changes in conductivity which may occur over a narrow interval of temperature. For this reason the curve through the experimental points has been drawn as a series of dashes in this region. The radial heat-flow method described below was subsequently used for a more detailed examination of the variation of thermal conductivity with temperature in the transformation region.

THE RADIAL HEAT-FLOW METHOD.

The experimental arrangement used for the absolute determination of thermal conductivity by a method involving radial flow of heat in a thick-walled cylinder is shown in Fig. 31.

The specimen, which was machined from

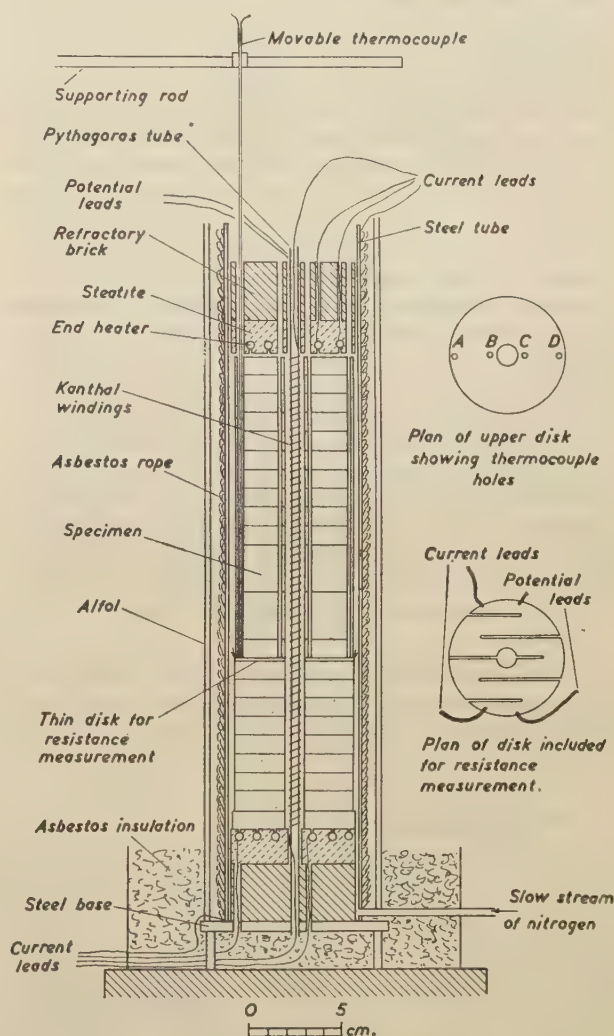


FIG. 31.—General Arrangement of Apparatus for Measurement of Thermal Conductivity by Radial Heat-Flow Method.

one of the 2.5-in. dia. bars of steel 7, which had been originally supplied for the determination of total heat, consisted of a number of superimposed disks, each 6.3 cm. in outer dia. and having an axial hole 1.1 cm. in dia. The two centre disks were each 2.54 cm. thick, and above and below these were, first, three disks, each 1 cm. in thickness, of steel 7 and then four similar disks of ingot iron. The main measurements were confined to the two thicker disks, the others merely serving as guards. In the two centre and upper seven 1-cm. disks, holes about 2 mm. in dia. were drilled (with a No. 48 Morse drill) parallel to the axis at four points, *A*, *B*, *C*, and *D*, on a diameter and about 2 mm. in from the curved surfaces. The disks were so aligned that a thermocouple, insulated by fine twin-bore silica tubing, could be moved up and down within any of the four sets of holes cut in the upper disks. With this arrangement it was possible to use one thermocouple for all temperature measurements, and to explore with it the temperature distribution in each of four positions within the specimen.

A thin disk of the steel, about 0.1 cm. in thickness, was included to enable check measurements of the electrical resistivity to be made from time to time. This disk was insulated from the main specimen by disks of mica. Its resistance was increased by suitable saw-cuts and could be determined by the usual method, which involved a reversal of the direction of the current to eliminate thermal e.m.f. As the effective dimensions of the resistivity specimen were not known, the readings were converted to specific resistivities from a knowledge of this constant at normal temperatures.

The subdivision of the thermal-conductivity specimen into disks was necessary to enable holes of sufficient depth to be drilled. This procedure, however, had a further practical advantage in that the poor contact between each pair of disks helped to diminish the flow of heat towards either end of the specimen. To eliminate completely this

longitudinal heat flow, small heating coils consisting of Kanthal wire set in grooves cut in steatite blocks were placed above and below the specimen. The axial heater consisted of Kanthal wire uniformly wound on a pythagoras tube about 7 mm. in external dia. Potential leads of platinum wire were tied on to the Kanthal heater at points about 5 cm. apart, the points of contact corresponding with the outer boundaries of the two central disks.

For tests made at temperatures below 350° C. the specimen was surrounded by a water-cooled steel tube of 7.1 cm. internal dia. and the temperatures were measured by means of a Nichrome and Eureka thermocouple. At higher temperatures the steel tube was heated by current generated in Kanthal wire uniformly wound on mica insulation. A slow stream of nitrogen was passed through the apparatus to prevent excessive oxidation, and a platinum/platinum-rhodium thermocouple was used for the temperature measurements.

During a test the end heaters were so adjusted that when a state of steady temperature was reached there was no appreciable gradient in temperature towards either end over the centre section. Temperature readings were then taken at six equidistant points within this section in each of the four holes, the same thermocouple being used for each observation. To enable the thermocouple to be readily held in the desired series of positions it was attached to a rod fixed to a carriage which could be moved up or down a graduated vertical column. The silica insulation ensured that the ball formed by the welded junction of the thermocouple was held approximately at the centre of each hole. From these readings the mean temperatures, T_1 and T_2 , for the internal and external positions were derived. The thermal conductivity, K , was then calculated by means of the equation :

$$K = \frac{VC \log_{10}(r_2/r_1)}{2.73dJ(T_1 - T_2)}$$

TABLE XXVIII.—*Typical Set of Readings Obtained Using the Radial Heat-Flow Method.*

Potential length, $d = 4.95$ cm.; mean value of $r_1 = 0.77$ cm. (holes *B* and *C*); mean values of $r_2 = 2.94_5$ cm. (holes *A* and *D*); current in central heater, 2.313 amp.; voltage drop across potential leads, 11.21 V.; energy generated in central section, 25.93 W.

Position (distance above lower potential point, cm.).	Thermocouple Readings, μ V.					
	<i>A.</i>	<i>B.</i>	<i>B - A.</i>	<i>C.</i>	<i>D.</i>	<i>C - D.</i>
0	2920	2949	29	2944	2916	28
1	2920	2951	31	2945	2916	29
2	2917	2950	33	2945	2917	28
3	2922	2951	29	2948	2920	28
4	2920	2953	33	2949	2921	28
5	2924	2953	29	2951	2923	28
Mean	2920.5	2951.2	30.7	2947.0	2918.8	28.2
Temperature, ° C.	365.3 ₇	368.6 ₄	3.2 ₇	368.1 ₉	365.1 ₉	3.0

where C is the current in the axial heater, V is the voltage drop across the central section, measured between points d cm. apart, and r_1 and r_2 are the mean distances of the two internal and two external thermocouple holes from the axis of the specimen. Division by J , the mechanical equivalent of heat, converts the thermal conductivity to the units previously employed, namely, g. cal./sq. cm./sec. for a thickness of 1 cm. and a difference in temperature of 1°C .

A typical set of results is given in Table XXVIII.

At a mean temperature of 366.8°C . the mean value of $(T_1 - T_2)$ is 3.13°C . and the thermal conductivity 0.085_5 .

The temperature differences employed for the evaluation of the thermal conductivity were quite small. They increased to about 6°C . at 700°C . and to 8°C . above the transformation point. At 308°C ., when a water-cooled furnace tube was used, the difference was 6.5°C .

The results obtained using this method are represented in Fig. 30 (marked \times). At the lower temperatures these values mostly lie a few per cent below the original curve, but are in good agreement at 700°C ., the region which it was desired to investigate in greater detail. The experimental data obtained in this region are set out in Table XXIX., and it is seen that a sudden

TABLE XXIX.—*Thermal-Conductivity Values Obtained near the Transformation Region by the Radial Heat-Flow Method.*

Mean Temperature, $^\circ\text{C}$. ($T_1 + T_2$)/2.	Temperature Difference, $^\circ\text{C}$. ($T_1 - T_2$).	Energy, W.	Thermal Conductivity, g. cal. cm. $^{-1}$ sec. $^{-1}$ $^\circ\text{C}^{-1}$
724.0	5.72	38.0	0.068 ₆
700.3	5.02	35.0	0.071 ₉
746.0	7.69	42.4	0.056 ₉
771.0	8.00	44.0	0.056 ₈
788.3	8.29	46.5	0.057 ₉
864.0	8.16	46.8	0.059 ₂

decrease in thermal conductivity occurs between 724° and 746°C .

Measurements of other properties have shown that the α - γ transformation occurs at about 730°C . for steel 7. The present results for the thermal conductivity of this steel are consistent with a sudden change in value from about 0.070 to 0.057, having occurred at about the same temperature. On the basis of these results the heavy line has been drawn in Fig. 30 to represent the change in thermal conductivity with temperature above 700°C .

Both methods agree in showing that whereas the thermal conductivity of the α -phase decreases with increase in temperature, that of the γ -phase increases. This type of change is consistent with the positive temperature coefficient possessed by

austenitic steels at normal temperatures, where the iron is also in the γ -form.

RESULTS FOR THE ELECTRICAL CONDUCTIVITY AND LORENZ FUNCTION.

Values have already been given in Section IIIA. for the electrical resistivity of steel 7 up to 1350°C . The additional measurements which were made in the course of the present experiment are not reported here in detail as they gave values in close agreement with those previously reported, and were obtained under less favourable experimental conditions. These measurements of electrical resistivity were included mainly as a ready means of ascertaining whether the properties of the steel had undergone any change as a result of the heat-treatment involved in the test. Thus, after thermal-conductivity values had been obtained up to a mean temperature of 974°C . by the longitudinal heat-flow method, some repeat points at lower temperatures gave values of the electrical conductivity about 3% greater than originally. A repeat determination of the thermal conductivity of this steel over the range 50 – 200°C . gave values which confirmed that a change had occurred in the steel, which had produced a similar effect on both conductivities.

The slow stream of nitrogen used in the radial heat-flow method was not sufficient to prevent considerable oxidation at high temperatures, as shown by a permanent increase in the resistance of the thin disk, and the partial closing of the thermocouple holes. In subsequent work it is proposed to conduct the experiment in an evacuated enclosure, and under these conditions it should be possible to extend the thermal-conductivity measurements to yet higher temperatures.

The variation of electrical conductivity with temperature can be seen from Fig. 32, where the

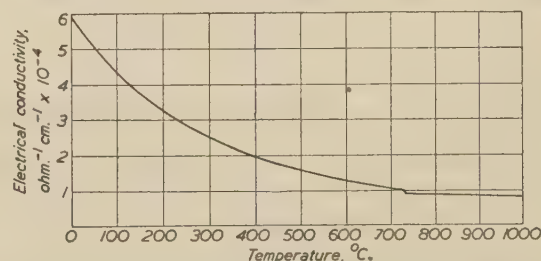


FIG. 32.—Variation of Electrical Conductivity of Steel 7 with Temperature.

reciprocals of the values previously given for the electrical resistivity of steel 7 are plotted. These values are also set out in Table XXX. which, in addition, contains values of the thermal conductivities, as read from Fig. 30, and the Lorenz functions (the thermal conductivity divided by the product of the electrical conductivity and the

TABLE XXX.—*Thermal Conductivity, Electrical Conductivity, and Lorenz Function of Steel 7.*

Temp., ° C.	Temp., ° Abs.	Thermal Conductivity, K , g. cal. cm. ⁻² sec. ⁻¹ °C. ⁻¹	Electrical Conductivity, σ , ohm. ⁻¹ cm. ⁻¹	Lorenz Function, $K/\sigma T$, $\times 10^8$.
0	273	0.119	58,930	0.74 ₀
50	323	0.118	50,610	0.72 ₂
100	373	0.115 ₅	43,180	0.71 ₇
150	423	0.112	37,370	0.70 ₉
200	473	0.108	32,450	0.70 ₄
250	523	0.103	28,490	0.69 ₂
300	573	0.099	25,110	0.68 ₈
350	623	0.095	22,210	0.68 ₆
400	673	0.091	19,790	0.68 ₃
450	723	0.087 ₅	17,770	0.68 ₁
500	773	0.084 ₅	15,910	0.68 ₇
550	823	0.081 ₅	14,310	0.69 ₂
600	873	0.078 ₅	12,950	0.69 ₄
650	923	0.075 ₅	11,740	0.69 ₆
700	973	0.072 ₅	10,690	0.69 ₇
720	993	0.071	10,300	0.69 ₄
740	1013	0.057	9,092	0.61 ₉
750	1023	0.057	9,045	0.61 ₆
800	1073	0.058	8,860	0.61 ₀
850	1123	0.059	8,710	0.60 ₄
900	1173	0.060	8,590	0.59 ₆
950	1223	0.062	8,490	0.59 ₇
1000	1273	0.064	8,395	0.59 ₉

absolute temperature) of the steel at temperatures ranging from 0° to 1000° C. A curve showing the variation of Lorenz function with temperature is given in Fig. 33.

It will be seen that the decrease which occurs in the thermal conductivity at the α - γ transformation is nearly twice as great as the corresponding de-

crease in electrical conductivity. Consequently there is an abrupt change in the Lorenz function from a value of 0.69×10^{-8} for the α -phase to a value of 0.61×10^{-8} for the γ -phase. The last-mentioned values are in reasonably good agreement with the value of 0.586×10^{-8} indicated by Sommerfeld's theory.¹⁵

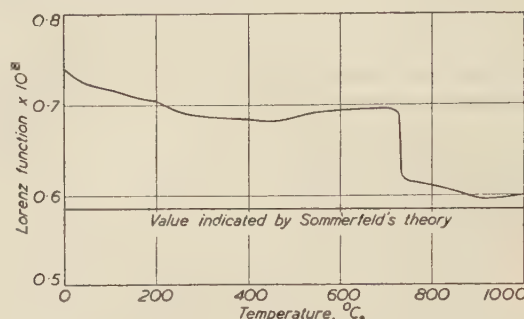


FIG. 33.—Variation of Lorenz Function of Steel 7 with Temperature.

It is of interest to compare the results now obtained for steel 7 with those obtained previously¹⁴ for an ingot iron of the following analysis :

Carbon, %.	Silicon, %.	Manganese, %.	Phosphorous, %.	Sulphur, %.
0.023	0.007	0.025	0.007	0.020

With this iron there was no marked change in the thermal-conductivity/temperature curve at the magnetic transformation point (circa 755° C.), the thermal conductivity continuing to decrease steadily to reach a minimum value in the neighbourhood of the α - γ transformation point (circa 900° C.). The addition of 0.8% of carbon thus appears to lower the temperature at which the thermal conductivity assumes a minimum value, and at the same time causes an appreciable decrease in conductivity to occur over a narrow range of temperature, which coincides with the transformation of the steel from the α - to the γ -phase.

Section III D.—Note on the Estimation of the Thermal Conductivities of Steels.

By R. W. POWELL, D.Sc., F.Inst.P.

INTRODUCTION.

At the time when results were published⁸ for the thermal conductivities and electrical resistivities of a series of steels up to temperatures ranging from 150° to 350° C., it was not foreseen that such a long period would have to elapse before it would be possible to complete the work up to high temperatures. So far it has only been possible to study the thermal conductivities of two of the steels, steel 7 (Section III C.) and steel 13 (Section III B.) to higher temperatures, but the electrical resistivities

of all of the steels have been measured (Section III A.) up to a temperature of 1350° C.

In the interim, data were requested for the thermal constants of certain steels to 1200° C. One object of the present note is to place on record the estimated values suggested for their thermal conductivities, and to explain the basis on which these estimates were made. The result of a very restricted analysis is also given regarding the dependence of the thermal conductivity of steels on the degree of alloying, which it is thought will give a clearer idea of the subject

and be of assistance when estimating the thermal conductivities of other steels.

ESTIMATION OF THE THERMAL CONDUCTIVITIES OF CERTAIN STEELS.

Early in 1941 data for the thermal conductivities up to 1200° C. of steels 2, 3, 5, 7, 9, 12, 13, and 19 were required in connection with calculations regarding the heating and cooling of steel ingots.¹⁶ Information regarding the thermal conductivity of steel 20 was later requested in another connection and the estimated results for this steel are also included.

At the time when the requests were received the electrical resistivities of the steels had been determined to 1350° C. and the thermal conductivity of one of the steels (7) had been determined to 1000° C.

For metals which obey the Wiedemann-Franz-Lorenz law, according to which the product of the thermal conductivity, K , and the electrical resistivity, ρ , divided by the absolute temperature, T , should have a constant value, L , a ready means is provided for the derivation of the thermal conductivity in terms of the known electrical resistivity. When the thermal conductivity is expressed in gramme calories per square centimetre per second for 1 cm. thickness and 1° C. difference in temperature, and the electrical resistivity is in ohm centimetres, the units normally employed in these reports, the theoretical value of the Lorenz constant, or function, is 0.586×10^{-8} .

Now, the data already published⁸ for the steels under consideration show them to have much higher values for the Lorenz function than this theory indicates throughout the range 0–350° C. At the same time the values so obtained are in general agreement, as regards the manner of their variation with temperature, with values given

previously⁹ to 800° C. for ingot iron¹⁷ and for four other steels.¹⁸ The subsequent extension¹⁴ of the results for ingot iron to 1000° C., together with the results obtained for steel 7 to a similar temperature, indicate that for iron there is a gradual decrease towards values of the theoretical order at 1000° C., and for steel 7 a sharp decrease towards this order occurs at about 730° C. This variation of Lorenz function with temperature has been published elsewhere.¹⁹

It is within this rather slender framework of experimental results that the curves for the variation of the Lorenz function with temperature of the steels in question have been extrapolated to give values up to 1200° C. Estimated values for the thermal conductivity were derived at intervals of 100° C. by means of the equation $K = LT/\rho$, using these extrapolated values for L and the previously reported values for ρ .

The values so obtained are given in Table XXXI. which, for the sake of completeness, also contains the experimental values previously determined.

When the estimates were made, the uncertainties in the extrapolated values for the Lorenz functions were not considered likely to introduce errors of more than about 10%.

The thermal-conductivity values given in Section IIIB. have since been obtained for steel 13, and it is possible to compare these results with the above estimated values for this steel. Steel 13 proved to be one for which the properties were dependent on heat-treatment. The estimated values were derived from the resistivity curve obtained on heating at a rate of 3° C./min. from the as-received condition, so they should be compared with the thermal-conductivity data for this condition. At 400° and 500° C. there is seen to be very close agreement, and at 600°, 700°, and 800° C. the estimated values have proved to be about 3, 4.5, and 6% high, respectively.

TABLE XXXI.—*Estimated Values for the Thermal Conductivity of Certain Steels*
(*g. cal. cm.⁻¹ sec.⁻¹ ° C.⁻¹*).

Temp., ° C.	Steel.								
	2.	3.	5.	7.	9.	12.	13.	19.	20.
0	0.142	0.124	0.124 ₅	0.119	0.087	0.079	0.031 ₅	0.116	0.102 ₅
100	0.138 *	0.122 *	0.121 *	0.115 ₅ *	0.090 *	0.081 *	0.033 ₅ *	0.111 *	0.102 *
200	0.127 *	0.117	0.115 *	0.108 *	0.093 *	0.084 *	0.039 ₅ *	0.106 *	0.100 *
300	0.118 *	0.110	0.109 *	0.099 *	0.094 *	0.085 ₅ *	0.043 *	0.101 *	0.097 *
400	0.109	0.102	0.100	0.091 *	0.088	0.085 ₅	0.046	0.092	0.093
500	0.098	0.094	0.091	0.084 *	0.084	0.080	0.049	0.085	0.087
600	0.088	0.085	0.081	0.078 *	0.078	0.073 ₅	0.052	0.076	0.081
700	0.079	0.076	0.072	0.072 *	0.063	0.067	0.054	0.069	0.074
800	0.068	0.062	0.059	0.058 *	0.060	0.064	0.056	0.062	0.063
900	0.064	0.063	0.061	0.061 *	0.063	0.066	0.058	0.064	0.065
1000	0.066	0.065 ₅	0.064	0.064 *	0.066	0.068	0.061	0.067	0.067
1100	0.068	0.068	0.067	0.068	0.068	0.070	0.064	0.069	0.070
1200	0.071	0.071	0.071	0.072	0.072	0.072	0.067	0.072	0.072

* Experimentally determined value.

Pending the completion of the experimental determinations of thermal conductivity, another way in which the reliability of the above estimates might be assessed is suggested below.

INFLUENCE OF COMPOSITION ON THE THERMAL CONDUCTIVITY OF STEEL.

When presenting the results for the first stage of this investigation, in which the thermal conductivities of the majority of the steels were determined up to 350° C., distinctive methods of plotting were adopted according to whether the steel had been classified as belonging to one of the three groups, carbon, alloy, or high-alloy steels (see Powell and Hickman,⁸ Fig. 166). Apart from

to 800° C.,¹⁸ but also includes the results of the recent determinations (Section IIIB.) made on steel 13. The uppermost curve is that for the ingot iron. Below this curve lie areas occupied by carbon steels, alloy steels, and high-alloy steels, respectively. The thermal conductivities of the alloy steels vary least with temperature and may possess small positive or negative coefficients in different ranges, as is seen for steels 9 and 12 in Table XXXI. The convergence towards fairly common values at high temperatures is clearly shown in both the table and the figure. Fig. 34 also suggests that the γ -phase is characterized by a positive temperature coefficient. This is valid, not only for those high-alloy steels which are in the γ -phase even from normal

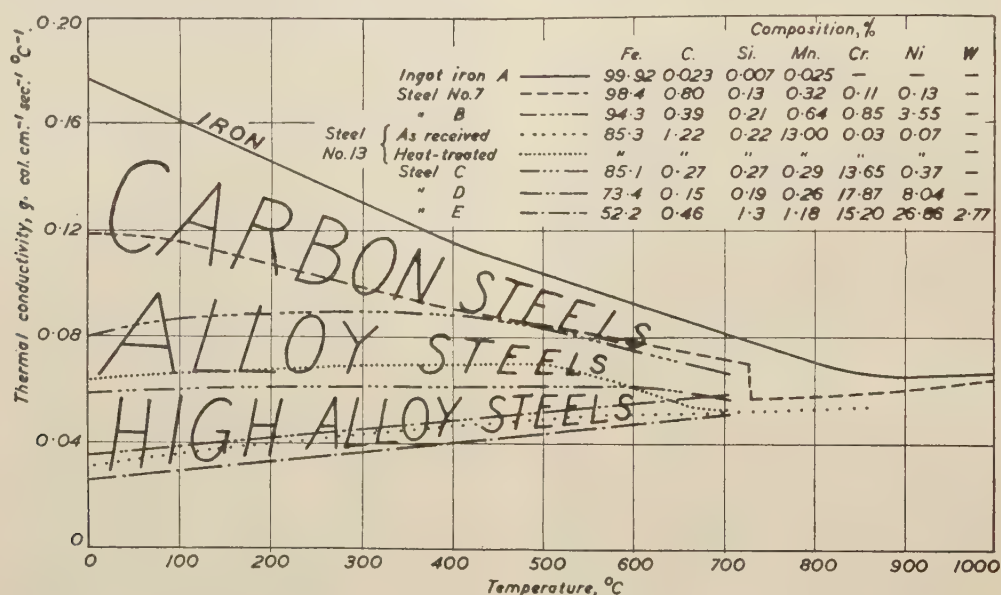


FIG. 34.—Variation of Thermal Conductivity of Iron and Steels with Temperature.

a little overlapping, the thermal conductivities decreased in the order in which the groups have been named. Furthermore, the temperature coefficients changed from negative for the carbon steels to positive for the high-alloy steels. These results therefore tended, over this restricted range of temperatures, to support the conclusions of an earlier survey⁹ of data available to 900° C., which showed the thermal conductivities of irons and steels to converge to values of between about 0.05 and 0.08 at 800° C.

Fig. 34 of the present report, which is similar to one of an earlier publication (Griffiths and others¹⁹, Fig. 17) gives a general idea of the anticipated variation with temperature of the thermal conductivities of steels of the three groups. This figure is again based largely on the aforementioned determinations on ingot iron¹⁴ and steel 7 to 1000° C., (Section IIIc.) and on four other steels

temperatures, but also for steel 7 and ingot iron as they attain the γ -state.

The important question as to the effect of chemical composition on the physical properties of steels is one which many workers have considered, and which has not yet been completely answered. It demands the study of specially prepared series of alloys rather than the somewhat diverse mixture of commercially important steels supplied for the present tests. The direct correlation of electrical resistivity and thermal conductivity against the number of atoms added to the iron was, however, examined when the estimated values for the thermal conductivity were put forward and these results lend support to the estimated values, and for this reason are detailed below.

This method of correlation is analogous to one originally adopted by Benedicks,²⁰ when he plotted

the electrical resistivities of a series of carbon steels against ΣC , the carbon values of the added elements, where

$$\Sigma C = C + \frac{12}{28} \text{Si} + \frac{12}{55} \text{Mn} + \&c.$$

C, Si, Mn, &c., representing the percentages by weight of these elements. To a first approximation Benedicks found that the electrical resistivity, ρ , in microhm cm., was given by :

$$\rho = 7.6 + 26.8 \Sigma C,$$

and the thermal conductivity, K , by :

$$\frac{1}{K} = 4.4 + 8.7 \Sigma C.$$

It is not to be expected that a simple correlation of this kind can be universally true. Benedicks' results were obtained for a series of carbon steels which contained only silicon, manganese, sulphur, and phosphorus in addition. The values of ΣC ranged up to only 1.8, or just over 0.9×10^{23} ,

additional atoms per 100 g. of the steel, and Norbury²¹ has since shown that the increment in resistivity of iron due to 1 at.-% of an element in solution increases the more remote that element is from the iron group of the periodic table. Yensen²², working with high-purity binary alloys, showed that the addition of very small amounts of carbon causes greater increases in the resistivity than is given by Benedicks' expression. Then, again, it is common knowledge that special heat-treatments can appreciably modify the physical properties of certain steels without the chemical composition as expressed in the above way being altered, although this last objection hardly applies to the present series of steels where the specimens were mainly tested in a well-annealed state.

In Fig. 35 the results obtained for the electrical resistivities of the present series of steels and also for ingot iron and the four other steels have been plotted for three different temperatures, 0°, 600°, and 1000° C., against the number of alloying atoms in 100 g. of the steel, that is, against $6.022 \times 10^{23} \Sigma$ (wt.-% of each constituent element/at. wt. of the element). The limitations of the method are clearly seen, a downward curvature of the line, shown dotted, being necessary to satisfy the points given by the high-alloy steels. The carbon steels at 0° and 600° C. tend to lie on a rather lower line, although the deviation is less marked at the higher temperature. At 1000° C., where the steels are in the γ -phase, a good linear relation holds for the carbon steels, but it is the alloy and high-alloy steels which now require a much flatter curve.

Incidentally, the slope of the curve at 0° C. is much less than was suggested by Benedicks' equation. An explanation may be that the steels he considered contained up to 0.86% of silicon, and it will be seen that the point for steel 21, which contained 1.98% of silicon, is well above the general curve, and that that for steel 6 which mainly differed from steel 5 in having 0.20% of silicon compared with 0.11%, is again a little displaced in this direction.

On plotting the corresponding results for thermal resistivity in this manner, large deviations from Benedicks' line are again obtained, the results at 0° C. for the less-alloyed steels being represented by the approximate line $1/K = 5.5 + 3.6 \Sigma C$. A wide departure is again apparent for certain steels, steel 21 again being well above the line, and the higher-carbon steels below it.

These plots of thermal resistivity have not been reproduced but, instead, Fig. 36 is given in which the thermal conductivities at 0°, 300°, and 600° C., respectively, have been plotted against the number of additional atoms per 100 g. of steel. Smooth curves have been drawn through each set of experimental points. The two steels which depart most from the 0° C. curve are 21 and 13,

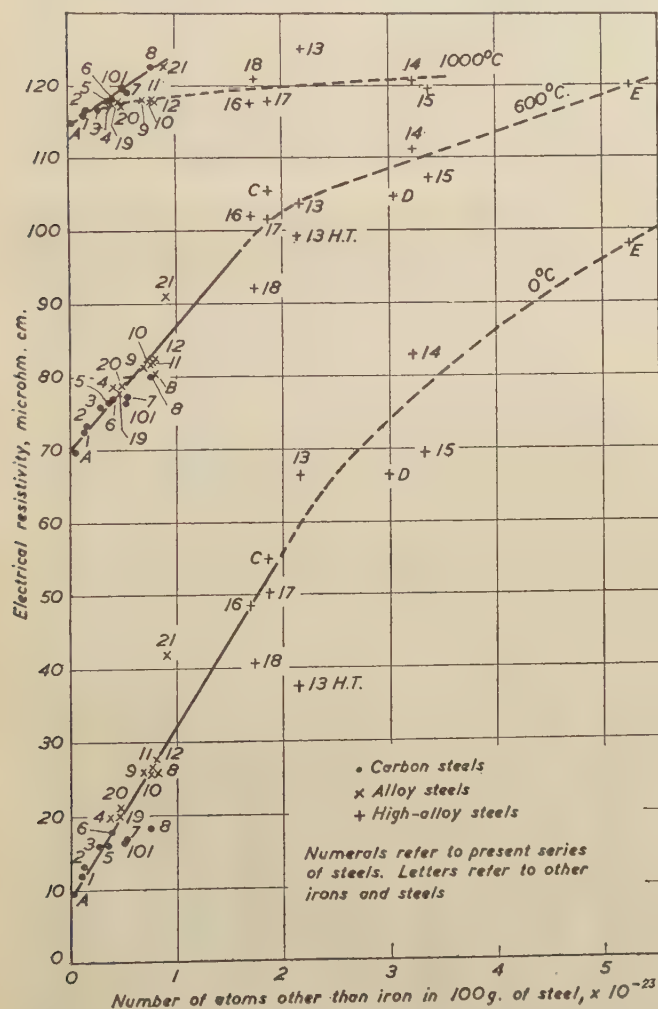


FIG. 35.—Electrical Resistivity of Iron and Steels Plotted against the Number of Added Atoms.

the latter being in the as-received austenitic condition. It certainly appears that silicon causes a greater decrease in the thermal conductivity of iron than do the corresponding atomic percentages of other elements. The fact that the

and that the deviations would appear likely to be still less at 600° C. The curve at 600° C. has been drawn to fit steel 7, ingot iron, and the four additional steels, for which experimental values were available at the time the other thermal-conductivity values given in Table XXXI. were estimated.

Of these steels, for which estimated values to higher temperatures were given, steel 13 was the only one which showed marked departures from the curves at 0° and 300° C. At 600° C. the estimated value for this steel in the as-received condition is just over 10% below the curve and less than 3% greater than the experimental value since obtained. Assuming that the thermal-conductivity values for these other steels also conform better to the curve suggested for 600° C. than does that of steel 13, then the present method of correlation gives an entirely independent means for checking the foregoing estimated values for these steels at this temperature.

These estimated values are shown as solid points in the lowest section of Fig. 36 and it will be seen that, apart from steel 13, only steel 19 departs from the curve by as much as 6% and the others all agree to within 2%.

On the basis of this analysis it seems unlikely that the aforementioned figure of 10% for the probable uncertainty of the estimated values will be exceeded in many instances. It should, however, be borne in mind that so far no experimental determinations have been made in conjunction with this investigation to temperatures above 1000° C.

For the sake of completeness, estimated thermal-conductivity values to 1200° C. have been derived by similar means for the remaining steels, 1, 6, 101,

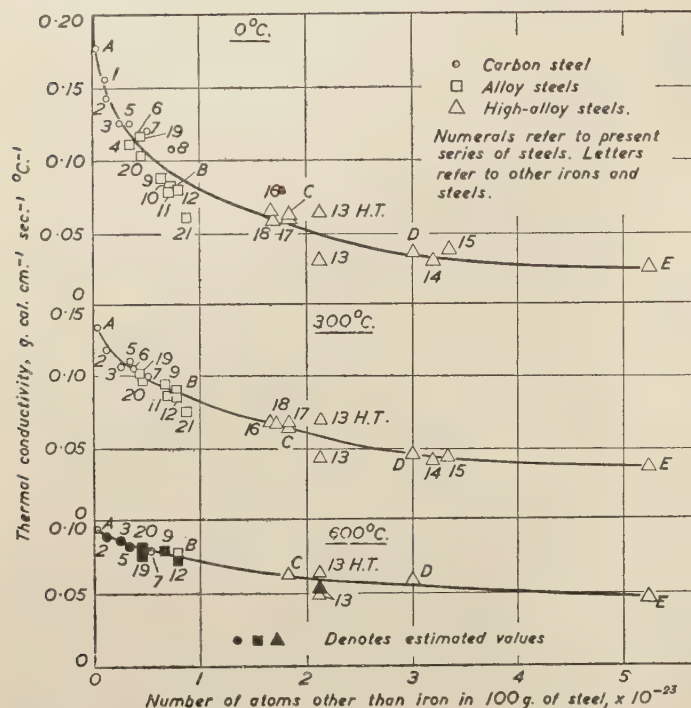


FIG. 36.—Thermal Conductivity of Iron and Steels at 0° C. (top), 300° C. (middle), and 600° C. (bottom), plotted against the number of added atoms.

heat-treated specimen of steel 13 gives a point well on the other side of the curve emphasizes the limitations of this method of correlation.

At the same time it will be seen that at 300° C. the points conform more closely to the mean curve,

TABLE XXXII.—Estimated Values for the Thermal Conductivities of the Remaining Steels of the Series (g. cal. cm.⁻¹ sec.⁻¹ °C.⁻¹).

Temp., ° C.	Steel.												
	1.	6.	101.	8.	4.	10.	11.	21.	14.	15.	16.	17.	18.
0	0.156	0.115	0.122	0.108	0.110	0.082	0.080	0.060	0.030	0.038	0.064	0.060	0.058
100	0.144*	0.115*	0.117	0.107*	0.110*	0.086*	0.085*	0.068*	0.035*	0.039*	0.066*	0.063*	0.062*
200	0.131	0.111*	0.110	0.104	0.107	0.088*	0.087*	0.072*	0.039*	0.041*	0.066*	0.065*	0.065*
300	0.121	0.105*	0.100	0.098	0.101	0.088	0.087*	0.074*	0.042*	0.043*	0.067*	0.066	0.067*
400	0.108	0.099	0.092	0.092	0.095	0.087	0.087	0.075	0.047	0.047	0.066	0.066	0.068
500	0.098	0.091	0.085	0.086	0.089	0.082	0.082	0.074	0.052	0.051	0.065	0.065	0.067
600	0.087	0.084	0.079	0.080	0.082	0.076	0.076	0.072	0.055	0.055	0.063	0.064	0.065
700	0.078	0.076	0.073	0.074	0.074	0.068	0.068	0.067	0.058	0.058	0.061	0.061	0.064
800	0.068	0.062	0.058	0.057	0.063	0.062	0.062	0.060	0.060	0.062	0.060	0.060	0.062
900	0.065	0.062	0.060	0.059	0.064	0.063	0.063	0.061	0.063	0.064	0.064	0.064	0.064
1000	0.066	0.064	0.064	0.062	0.065	0.066	0.066	0.063	0.066	0.067	0.066	0.066	0.066
1100	0.068	0.067	0.068	0.065	0.068	0.069	0.069	0.066	0.068	0.069	0.069	0.069	0.068
1200	0.071	0.071	0.071	0.068	0.071	0.071	0.071	0.070	0.071	0.071	0.073	0.072	0.070

* Experimental values.

8, 4, 10, 11, 21, 14, 15, 16, 17, and 18. These values are set out in Table XXXII.

The experimental determinations of the thermal conductivities of this series of steels are being continued, primary consideration being given to detailed examination of the transformation regions and to the extension of the investigation to as high a temperature as possible. The data so obtained will serve to check the foregoing estimated values in the regions where they are thought most liable to be in error.

Before concluding this section it is thought that some reference should be made to cases where an estimate is required regarding the thermal conductivity of a steel for which no guidance as to the values of the Lorenz function is available from determinations at lower temperatures. If the composition of the steel is similar to that of one of the present series, probable values for the Lorenz function at these temperatures can be deduced from those given in Table LIV. of the previous report.²³ A more general idea of the dependence of the Lorenz function on the nature and composi-

different lines, according to whether they are in the α - or γ -state. Much higher values are obtained for the α -irons and, when plotted in this way, the Lorenz functions of steels 16 and 17 no longer appear to be anomalous. Furthermore, the change in Lorenz function of steel 13 as a result of heat-treatment is seen to be consistent in direction, but not in magnitude, with the observed formation of the α -phase. Steel 18, containing 18% of tungsten, occupies a mid-way position as it did when the attempt was made to correlate specific-heat and expansion data in a somewhat analogous manner (see Fig. 4). If the composition of the steel is known, allowances can be made for such departures as are indicated in Fig. 37.

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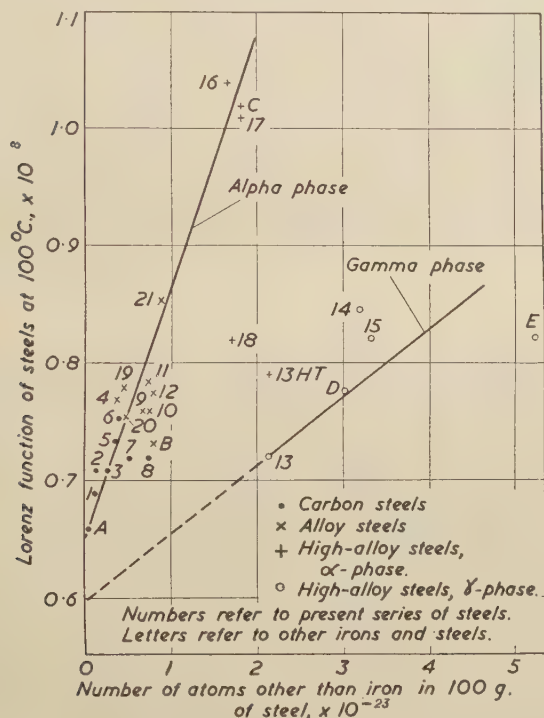


FIG. 37.—Lorenz Function of Steels at 100° C. Plotted against the Number of Added Atoms.

tion of the steel can be obtained from Fig. 37, where the Lorenz functions at 100° C. of the steels considered in this report are also plotted against the number of additional atoms in the steel. The considerable degree of scatter again indicates this method of correlation to be only a very rough approximation. At the same time it is clearly seen that the steels tend to conform to two

NEUMANN BANDS AND THE PLANAR-PRESSURE THEORY OF HYDROGEN EMBRITTLEMENT.*

By CARL A. ZAPFFE, M.S., Sc.D. (BALTIMORE, MD.).

(Figs. 1 to 17 = Plates X. to XIII.)

SYNOPSIS.

In a broad review of published work on Neumann bands, reason is found for disbelieving the present accepted theory that these bands represent primarily a twinning phenomenon. A study of Neumann bands in ingot iron and in silicon ferrite with the new micrographic technique known as fractography confirms this doubt. A new theory is offered based upon the rôle of visible planar imperfections seen in fractographs.

To test the theory, the passage of hydrogen gas through these irons is studied both before and after deformation by observing the effusion of the gas under oil. The observations provide proof that not only Neumann bands but also slip lines are based on and located by a pre-existent "planar imperfection structure" which must hereafter be considered in all studies of mechanical deformation, and also chemical precipitation.

The sudden appearance of the hydrogen bubble, its constant size, and the confinement of its appearance to bands and slip markings, simultaneously afford proof for the fissured structure of these bands and for the planar-pressure theory of hydrogen embrittlement advanced earlier by the author.

The conclusion is drawn that deformation bands in general comprise primarily a shearing movement of adjoining mosaic sections, and that the material within the zone of shear has a mathematical probability for twinning which varies from approximately 1.0 in metals such as bismuth and zinc to virtually 0.0 for certain other metals. In spite of the unlikelihood of twinning in body-centred-cubic structures, a iron is known definitely to twin under certain conditions. Hence Neumann bands may be twinned or they may not, their condition with respect to twinning not being fundamental to an understanding of the band phenomenon.

INTRODUCTION.

SINCE Neumann's original discovery in 1848 that the geometric markings in the kamacite of meteoric iron from Braunau were not Widmanstätten figures, as was previously thought, there proceeded a surprising amount of published argument on the nature of these markings.

Introduced first among mineralogists, Neumann bands were immediately assigned to the same twinning mechanism that produces similar markings in fluorspar. There the markings are known to be either contact twins formed from a simple revolution of 180° around the twinning axis, or twins of the interpenetrating-cube type formed according to the Spinel law. The twinning plane is $\{111\}$ and the trigonal axis is the axis of twinning, the bands occurring parallel to the junctions of the faces of the interset cubes. This argument was opposed vigorously for some time, but is now accepted by many metallurgists in almost its original form.

Certain investigators, however, have advanced attractive reasons from time to time for questioning this classical concept; and careful study of

published investigations actually reveals an uncertainty about the nature of Neumann bands which is not in keeping with the popular tendency to regard the matter as settled.

The present paper therefore has three principle purposes: (1) To review exhaustively the extant literature on Neumann bands so that the present status of that phenomenon can be re-evaluated; (2) to apply the technique of fractography to the direct study of Neumann bands; and (3) to obtain information on the internal structure of the bands by studying their inter-relationships with diffusing hydrogen.

THE HISTORY OF NEUMANN BANDS.

Crystallography.

Among such early writers as Tschermak,¹ Sädebeck,² and Linck,^{3,4} the principal argument over Neumann's discovery concerned the crystallography of the phenomenon and whether it occurred through deformation or in the original crystal growth. A classic research by Osmond and Cartaud,^{5,6,8} during the years 1904-1907, on

* Received January 15, 1946.

the meteoric irons of Timbuktu and Caille consummated that difference of opinion by demonstrating that the phenomenon developed only through mechanical deformation and that the markings lay on the icositrahedral {112} planes as surmised earlier by Linck.³

Osmond and Cartaud, themselves speaking of Neumann "lines" in 1904,^{5,6} called them "lamellæ" in 1907⁸ after showing that the phenomenon was three-dimensional and plate-like. Howe¹⁹ ultimately gave them the name of "bands."

Occurrence.

Neumann bands were first observed in terrestrial irons by Prestel.⁴ Subsequently, Hadfield,⁷ Stanton and Bairstow,⁹ Robin,¹⁰ Matwieff,¹¹ Portevin and Durand,¹² Potter,¹³ and several others,^{21, 26, 39, 45} reported having found the bands in such variegated materials as Swedish iron,^{7, 9} soft basic steel,^{10, 11} silicon steel,^{19, 52} manganese steel,^{13, 19, 20} possibly brass and bronze,^{32, 48, 49} aluminium and copper,^{33, 34, 50} zinc,^{35, 38} and magnesium.⁴³ Conditions within the crystal unfavourable to slip, which seem prerequisite, were obtained in various ways, *e.g.*, by using sub-zero temperatures, by alloying elements such as silicon and phosphorus—but not carbon—and by deformation due to shock. In fact, preliminary deformation producing slip precludes the formation of Neumann bands²⁵; and there is an upper temperature limit beyond which slip occurs to the exclusion of Neumann bands.^{10, 45} Also, a critical minimum of ferrite is necessary, occurrence of the bands in carbon steel being affected adversely by a variation of as little as 0.05% of carbon.²²

Evidence in Favour of Twinning.

With the original impetus in favour of the argument that Neumann bands are twins, the findings in phosphoric iron in 1924 by Harnecker and Rassow²³ of etch-pits having a twin relationship with the matrix would seem decisive. Furthermore, Pfeil^{30, 37} reported small bands properly changing direction as they crossed larger ones; and Mathewson and Edmunds⁴¹ (after first granting in a previous paper that grounds for a controversy existed⁴⁰) provided X-ray evidence of twin relationships within the band, which they believed should at last settle the controversy.

Smith, Dee, and Young,⁴⁴ in a long and convincing paper, demonstrated that the Neumann bands in Coahuila meteorites were twins; Millington and Thompson³⁶ reversed their earlier decision²⁴ and admitted that twinning on {112} by rotation of a cube about its trigonal axis satisfies known data; and O'Neill²⁹ gave the following five reasons for regarding these bands as twins:

- (1) Their sides are often parallel.
- (2) They deflect slip bands.

(3) They etch differentially, suggesting a characteristic orientation.

(4) Parallel bands have identical orientation.

(5) Production of a twinned layer by deformation of ferrite along {112} planes seems simple and reasonable.

Barrett, in his recent book,⁵⁰ accepts the explanation that Neumann bands are twins.

Evidence Against Twinning.

While the conclusion reached by these investigators is admittedly convincing for the particular specimens under their observation, certain facts and observations recorded by other investigators using other specimens remain definitely and suggestively at variance. For example, Rosenhain and McMinn²⁵ provide strong evidence against twinning in their specimens by showing utterly irregular crossings of Neumann bands by slip lines, entirely unlike the behaviour of twinned copper; and Portevin and Durand¹² found that etch-pits in the bands of their specimens had the same orientation as the matrix, though Howe¹⁹ points out that they might have etched through the thin band and into the matrix. Yap³¹ reports having obtained Neumann bands in a bent piece of Armeo iron on the tension side only, which can be significant.

In manganese steels deformation lines similar to Neumann bands occur, but Howe and Levy²⁰ give five reasons why they should be considered slip bands and not twins. While narrow deformation bands occur in bismuth, tin, and zinc, which are truly twin bands,¹⁵⁻¹⁸ there is a similar structure in aluminium which crystallographically has no relation to the adjoining crystals.³³ There is a specious "twinning" in 5% aluminium-copper alloy which is simply two parts of one crystal which has been separated by shear. Furthermore, although α iron does stand as a verified exception among body-centred-cubic metals in developing true twins under certain conditions,^{42, 46} those twins have virtually no physical resemblance to Neumann bands.

Mention might also be made of Thompson and Millington's theory²⁴ that Neumann bands are not twins, but are zones of a new lattice set up by slip movement, for example, on two parallel sets of (110) planes intersecting at [112] and there changing their atomic packing to face-centred-cubic.

Separation and Strain in Neumann Bands.

Even those postulating twin relationships grant that a strong degree of disorganization and strain exists, particularly at the boundaries of the band.^{23, 40, 44} Osmond and Cartaud⁸ showed long ago that etching first attacks the junction planes, and that polishing to low relief actually results in

a slight depression on a cube face. Portevin and Durand¹² found etching sufficiently preferential to depress the band; and Tammann¹⁴ suggested that iron is actually made more corrodable by the presence of Neumann bands.

In an outstanding research on producing Neumann bands by detonation of explosive charges, Foley and Howell²² first state that the bands are not preferentially etched; but in a later paper by Foley and Crawshaw²⁷ a quantitative test is actually used with some success in which a fixed area of the specimen is exposed to HCl under controlled conditions, and the dissolved iron is titrated to give a measure of the band content.

Krivobok²⁸ regards Neumann bands as principal seats of strain and makes no attempt to provide any further definition; he traces recrystallization in iron and silicon ferrite to Neumann bands—a fact now generally accepted.

THEORY OF NEUMANN BANDS.

Three outstanding conclusions result from a study of these published investigations:

(1) There seems to be reliable evidence that Neumann bands studied in several investigations were twins.

(2) There likewise seems to be strong evidence that the Neumann bands studied by several other investigators were not twinned.

(3) It is universally agreed that there is severe disorganization and strain within the banded zone.

If these conclusions can be compromised instead of eliminating one of the first two, an answer is attainable. Greninger⁴⁶⁻⁴⁹ (in the author's opinion) indicates the solution when he suggests that intragranular surfaces play the leading rôle in twinning. Macromosaic structure and block movement are the terms he uses; and he assumes that twins form from crystalline disturbances such as mosaic separations, in contrast to the classical theory based on uniform crystallographic reorganization. He further points out that the angle made by deformation markings with respect to the crystal may be contained in the plane of movement, or that angle may result from a composite movement having directional components differing from that of the basic movement.

Although Mathewson⁵¹ does not believe that blocks such as those separated by Zwicky's hypothetical "Pi" planes⁵³ of mosaic structures can twin, Greninger's postulate remains attractive for at least two reasons:

In the first place, proof for a mosaic condition which affords inherent internal surfaces or separations in all crystals yet known to metallurgists is a *fait accompli*, recognition of which by

metallurgists is long overdue. Internal surfaces are already there, and any worthwhile theory regarding deformation of any sort requires to start at that point.

Secondly, recognition of the mosaic condition of the crystal provides a compromise of the foregoing arguments. That is, the deformation producing a Neumann band can be understood to accomplish primarily a shearing motion of two crystal portions along a zone of pre-existent surfaces in the mosaic structure which is thin because of a resistance to, or lack of time for, propagation of widespread slipping. The development and limitation of this zone is consistent with the preferred occurrence of banding in materials and under conditions allowing only limited slip.

As a result of the high and localized deforming force acting on a lattice having a possible twinning reorganization, a secondary response to the pressure is thereby enabled, the accomplishment of which has a probability varying considerably for the materials under discussion and often being appreciably less than 1.0.

The Neumann band then really becomes a phenomenon which does not necessarily belong either to a twinning operation or to pure slip. One end member in the series of possible deformation structures, with a twinning probability close to 1.0, is the deformation band known to be twinned in such metals as bismuth, tin, and zinc. The other end member, with a twinning probability close to 0.0, is the band known to comprise only slip in some of the metals previously discussed. There is significant confirmation of this hypothesis in the fact that Howe,¹⁹ in discussing his famous "X-bands", describes as many as eight categories within the phenomenon of deformation bands.

EXPERIMENTAL.

To test this theory, two new and interesting methods are available. First, with the technique of fractography⁵⁴⁻⁵⁶, Neumann bands can be observed in their nascent and untouched state for studying twin and crystallographic relationships, and for observing their disposition within the intragranular imperfection structure. Secondly, from the phenomena attending the absorption and diffusion of hydrogen through steel, the assumption of the internal surface operative in the deformation bands can be proved.

Fractographic Study of Neumann Bands.

Neumann bands are conveniently studied by fractography because they are associated with brittle fractures. In addition to several materials already available for this study, Dr. C. S. Barrett, of the Carnegie Institute of Technology, kindly supplied a sample of 4.96% silicon ferrite from

the material used by him in his research on slip and twinning.⁵⁷ A conventional photomicrograph of this silicon ferrite in Fig. 1 shows flat-lying Neumann bands as they appear after polishing and etching a previously deformed specimen.

Fig. 2, a photomicrograph at high magnification of a specimen deformed after polishing and etching, shows the distinct sloping nature of the original bands, visually suggestive of simple faulting or shearing. This "step" appearance was also observed by Pfeil.³⁰ The figure provides a clear example of "fish-tailing"^{25, 30} and of intersection with an inclusion. In meteorites, intersection of a Neumann band with a thin rhabdite crystal often results in its breaking,^{3, 44} illustrating the occurrence of a major movement of the crystal portions such as is shown here.

The original photograph shows that the faintly visible slip lines at 40° to the bands do not change direction within the band, but simply show displacement commensurate with the apparent faulting. Of course, as Pfeil points out,³⁰ the numerous directions available to slip in ferrite lessen somewhat the significance of this observation.

In Fig. 3, a fractograph clearly reveals the trigonal symmetry of the banding; and Fig. 4 presents a most interesting instance of a combination of at least three crystallographic phenomena. Since the cleavage plane here can be assumed to be (001), most of the markings on the fractograph can be tentatively identified. For example, the vertical fissure through the V is undoubtedly a (100) cleavage; the Neumann bands are at 34° to this cleavage which is consistent with the {112} habit. Other markings are also visible which closely resemble the striae seen in bismuth and rock salt.⁵⁵ Here the striae can be identified as {110} registrations by the angles of 0° , 45° , and 90° that they make with the cleavages. Slip in this material is known to occur on {110}.⁵⁷ The top of Fig. 4, not apparent in the reproduction, is a cleavage edge.

From other fractographs (not reproduced here) the trapezohedral habit of the bands was closely established by measuring the angle with a cleavage edge and then rotating the specimen through 90° to bring the adjacent cleavage face into focus. The angle of the outcrop of these same bands on that second face verified the indices of the plane as {112}.

For comparison, a specimen of purified electrolytic iron fractured at the temperature of liquid air is shown in Fig. 5. Note the disposition of the markings with respect to the cleavage edge (lower left). While the rectangularity evident in this specimen was not generally observed in silicon ferrite, {112} planes include 90° intersections on {100}. That these bands have essentially the

nature of faulting of adjoining crystal sections is shown clearly in the fractograph of Fig. 6 taken with oblique light from the left. A V-shaped block of metal of which the boundaries are Neumann bands has visibly sheared into the body of the specimen, allowing one shear wall to be illuminated and the other to be shaded. The two fractographs in Fig. 7 (taken with oblique light from opposite sides) show this even more clearly. In one case the slope casts a shadow out upon undeformed metal, and in the other the slope is so illuminated that it reflects upon the base. Although the angle of this slope was not measured accurately, at cleavage edges it appeared always to show approximately one of the $145^\circ/35^\circ/55^\circ$ angles belonging to the habit of {112}/{100}. A marked difference exists between these steep registrations and the frequently flat-lying and truly twinned deformation bands of antimony and bismuth shown in Fig. 8. This difference is in agreement with the present hypothesis in which the primary action in the specimen of Fig. 6 is a shearing or faulting movement of the V-shaped block into the body of the crystal. Twinning certainly may occur, but whether the material immediately bounding the plane of movement is twinned or only disorganized seems to be a purely secondary and not a fundamental consideration.

In Fig. 6, also, wandering lineage markings can be seen to traverse the slope unaffectedly. The fractograph in Fig. 9 shows this relationship with the lineage structure even more clearly. Since the interdependency of lineage and twinning is not yet understood, however, the failure of these markings to change direction on entering the shear wall, or "band", does not necessarily constitute proof against twinning within the band.

Purified electrolytic iron is shown again in Fig. 10. In this case the specimen was embrittled by cathodic hydrogen and fractured at room temperature. This fractograph (which has been taken slightly out of focus to display the lamellar characteristics of the facet) shows that the presumed Neumann "bands" dissolve into a simple faulted region of no appreciable thickness when the third dimension is taken into account. The multiple lines, incidentally, are for the most part not effects of birefringence, but are lamellar edges which can be focused individually.

In the light of the imperfection theory of crystal structure, these bands can be understood to be simply a shear surface bounded by a thin disorganized zone of mosaic elements which may be lamellar or block. There is no evidence of displacement of the traversing slip lines, though many do not succeed in crossing that zone, as would be expected if it were sufficiently disorganized. Rosenhain and McMinn²⁵ similarly observed that the band acted as an obstacle to intersecting slip lines, which only the largest succeeded in crossing.

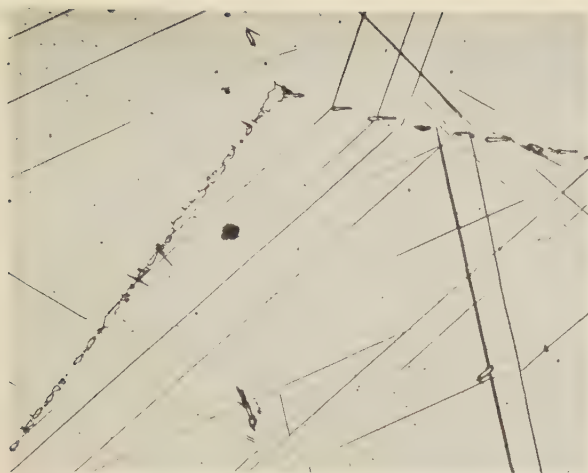


FIG. 1.—Specimen Deformed before Polishing and Etching.
× 250.

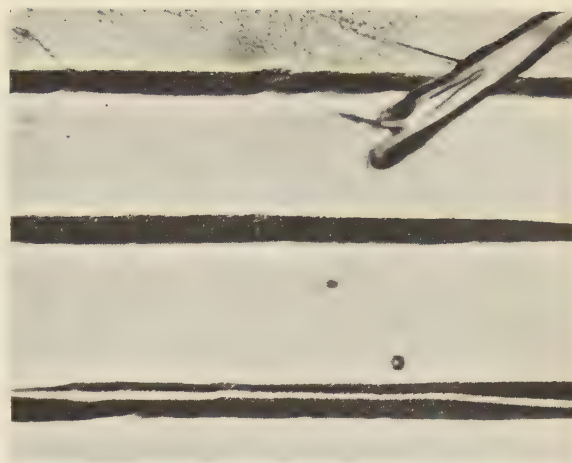


FIG. 2.—Specimen Deformed after Polishing and Etching.
× 2000.

FIGS. 1 and 2.—Conventional Photomicrographs of Neumann Bands in Silicon Ferrite.



FIG. 3.—Fractograph of Silicon Ferrite ((100) Facet), showing the trigonal symmetry of Neumann Bands. × 750.



FIG. 4.—Fractograph Showing Neumann Bands in Combination with Slip and Cleavage Markings. × 300.

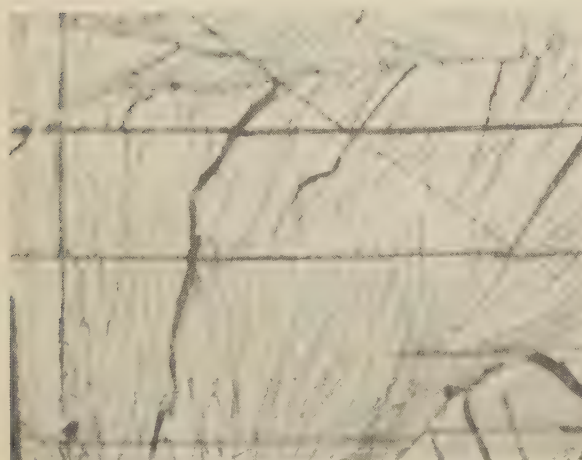


FIG. 5.—Purified Electrolytic Iron Fractured at the Temperature of Liquid Air. × 500.

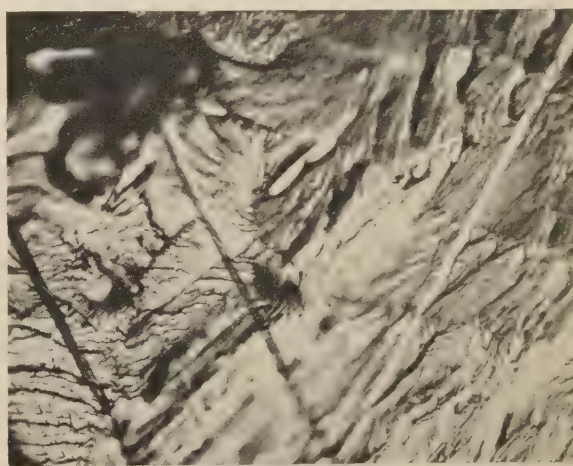


FIG. 6.—Inward Shearing Movement of a V-Shaped Block of which the Boundaries are Neumann Bands. × 1000.

[Zapffe: Neumann Bands.

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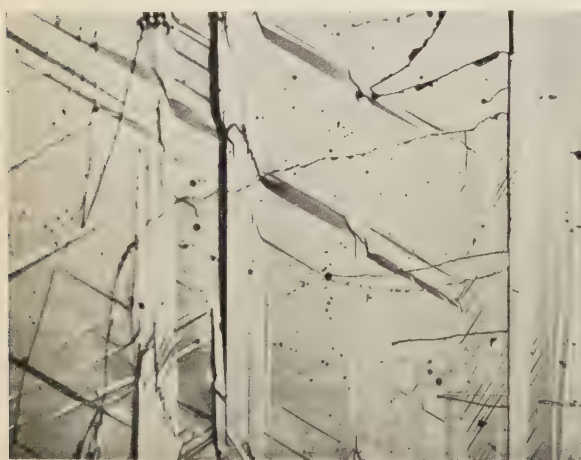


(a)

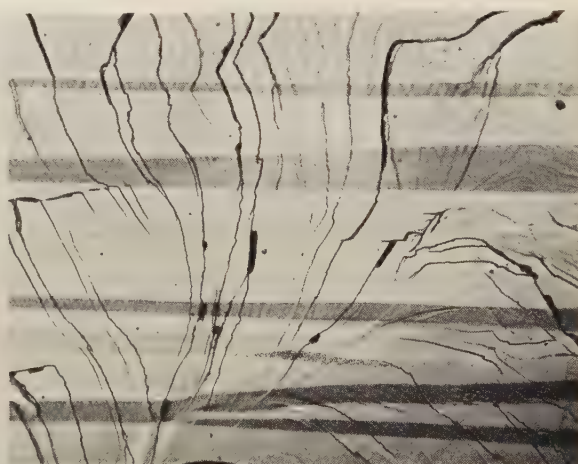


(b)

FIG. 7.—Identical Fractographs Taken with Opposite Oblique Illumination; illuminated (a) from the left, and (b) from the right. $\times 1000$.



(a)



(b)

FIG. 8.—Fractographs of Deformation Bands Known to be Twins in (a) Antimony ($\times 200$), and (b) Bismuth ($\times 500$).

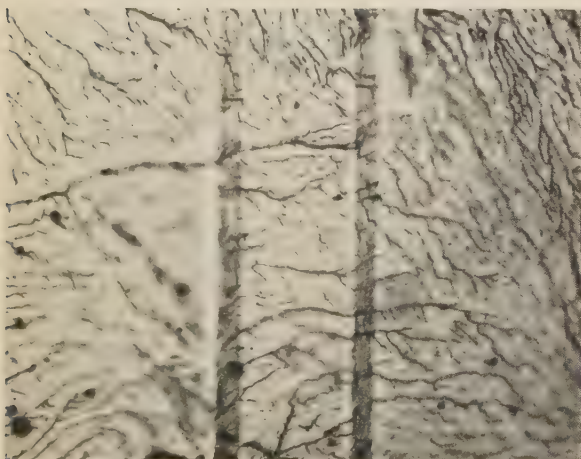


FIG. 9.—Fractograph Showing Relationship between Neumann Bands and Surface Lineage Markings. $\times 1000$.

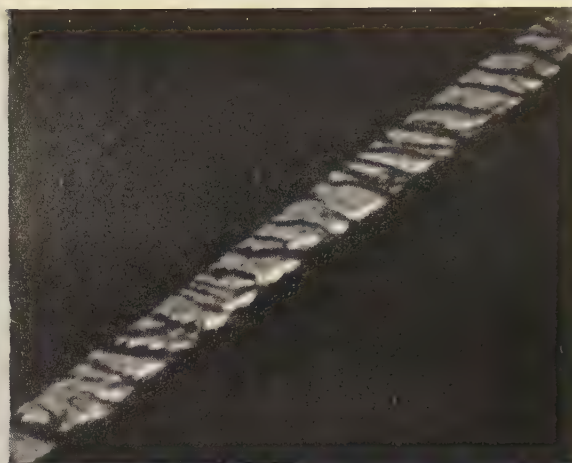


FIG. 10.—Purified Electrolytic Iron Embrittled by Cathodic Hydrogen and Fractured at Room Temperature. $\times 350$.

[Zapffe: Neumann Bands.]



(a)



(b)

FIG. 11.—Fractographs of Neumann Bands in Silicon Ferrite, showing the planar imperfection structure; (a) $\times 2000$, and (b) $\times 4000$.



FIG. 12.—Hydrogen Bubble Trapped in Balsam after Issuing from the Intersection of a Neumann Band and a Fractured Inclusion. $\times 2000$.

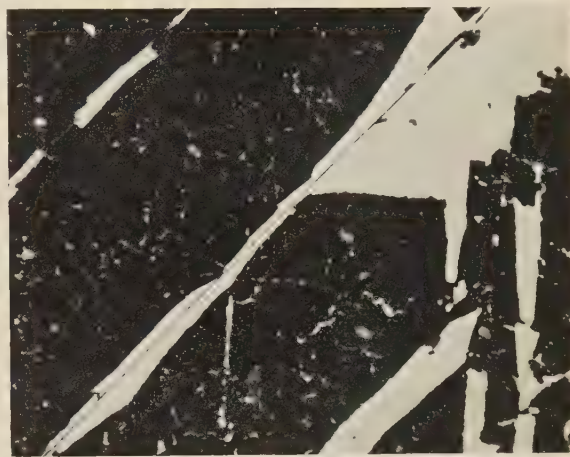


FIG. 13.—Photomicrograph Illustrating the Apparent Resistance to Cathodic Etching at Band Zones. $\times 200$.

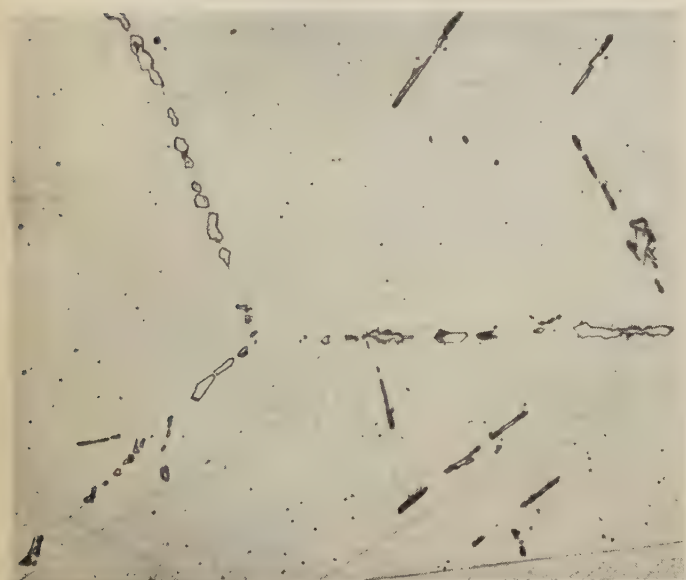


FIG. 14.—Sample of Silicon Ferrite, showing Widmanstätten type of precipitate. Etched with HNO_3/HF mixture. $\times 250$.

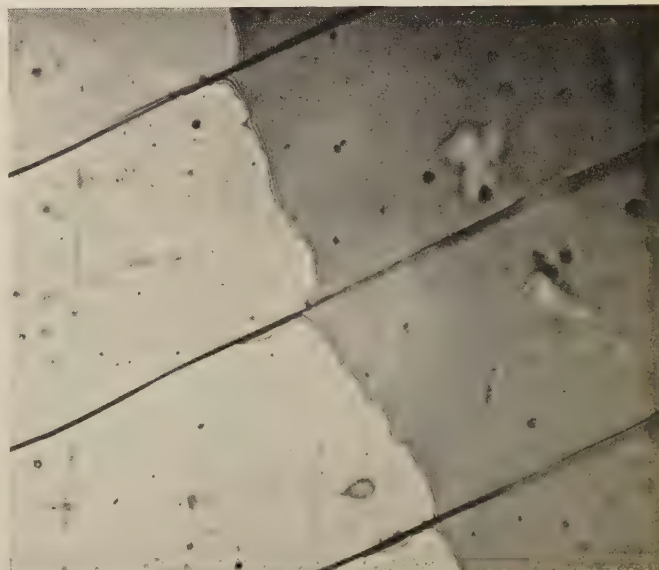


FIG. 15.—Film of Canada Balsam on Banded Specimen, showing preferential wetting of the bands. $\times 350$.

[Zapffe: Neumann Bands.]

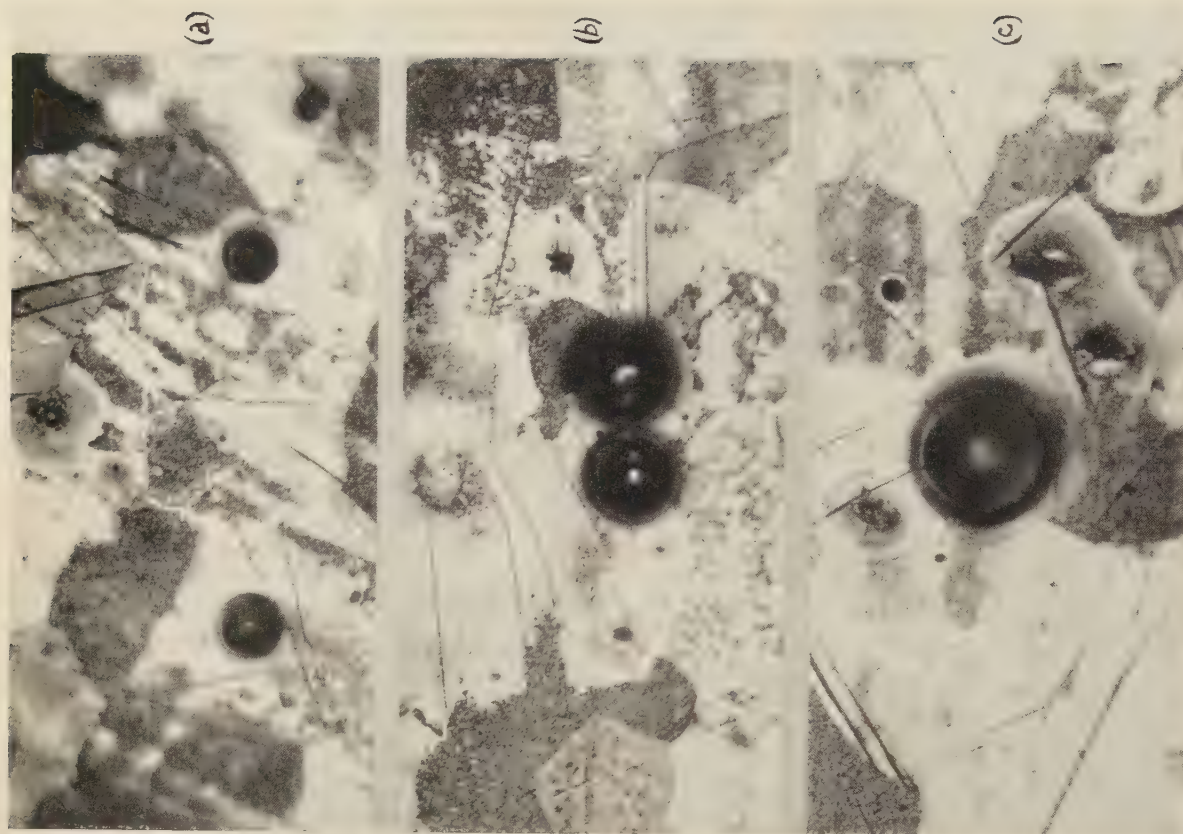


FIG. 17.—Samples of Armco Iron, showing hydrogen bubbles issuing from traces of deformation planes, (a) and (b) $\times 500$, and (c) $\times 2000$.



(a)



(b)

[Zapffe: Neumann Bands.
[To face p. 127 P.

FIG. 16.—Hydrogen Bubbles in Canada Balsam just after Issuing from Neumann Bands. $\times 200$.

They also stated that Neumann bands frequently appear to be a bundle of fine slip lines; this is consistent with the present observations.

The fractographs shown in Fig. 11 are especially interesting in making obvious the planar imperfection structure. The plainly visible platelets are of the order of thickness (approximately 0.5μ) commonly ascribed to the postulated mosaic unit block. Since these platelets and their dimensions are common representations of practically every structure and pattern observed in fractography⁵⁴⁻⁵⁶, as well as in other studies concerning intragranular structure,⁵⁸ they certainly stand as the strongest kind of evidence for the theory of imperfection structure, and, in addition, they have much significance in the understanding of the deformation phenomenon known as the Neumann band. That is to say, the postulate that the Neumann band is fundamentally a phenomenon of shear properly raises the matter of identifying the shear plane. The simplest identification is $\{112\}$, and there is evidence in favour of this. Against it, however, is the fact that slip is more common on $\{110\}$ in these materials. Recalling Greninger's suggestion of composite slip forcibly brings one's attention to the lamellae in Fig. 11. These lamellae very plainly may lie along a plane such as $\{110\}$; and the band itself then follows $\{112\}$ in the nature of a staircase whose steps comprise slip on $\{110\}$ on a mosaic scale.

BEHAVIOUR OF HYDROGEN IN BANDED IRON.

The Planar-Pressure Theory of Hydrogen Embrittlement.

Principles of Pressure.

According to well-established principles, hydrogen gas enters metals in the atomic form only; it diffuses through the lattice as atomic hydrogen, or as H^+ ions only, and the quantity of that element held in the lattice is a function of both temperature and pressure. At any given temperature the solubility conforms to Henry's law:

$$[H] = k(H) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $[H]$ and (H) are the respective fugacities of atomic hydrogen in solid solution and in the contiguous gas phase. For iron, there is, as yet, no known solubility limit in the true sense, only conditional limits existing when pressure is fixed.

Because of the established gaseous equilibrium between atomic and molecular hydrogen, the solid solution can be related to the common gaseous form (H_2) as follows:

$$[H] = k'(H_2)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

from which, in turn, the limiting potential pressures of H_2 in a gas phase contiguous to a solid

solution prepared from atomic hydrogen, as in pickling, can be approximated to:

$$P_{(H)} = k''[H]^2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Since the partial pressure of atomic hydrogen in thermal equilibrium with 1 atm. of molecular H_2 at ordinary temperatures is an infinitesimal number, equation (3) reveals the possibility that virtually unlimited pressures of H_2 may be derived from Fe-H solutions formed from pickling operations where $P_{(H)}$ itself approaches 1 atm. Borelius and Lindblom,⁵⁹ for example, developed experimentally for the case of cathodic pickling an expression which—large as the $P_{(H)}$ values are—must yet lie on the low side. The expression is:

$$P_{(H)} = 17,000I \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where I is the current density in amp./sq. cm., and P is in atmospheres.

Planar Mosaic Openings.

As a consequence of these principles, gaseous H_2 must evaporate into and collect at every hiatus within the metal lattice. This action partitions the dissolved gas into an atomic portion remaining dissolved in the lattice and a much greater portion occluded physically under high pressure as molecular or quasi-molecular hydrogen. According to knowledge of mosaic structure, and information in this paper, there is a vast inherent and crystallographic network of thin planar separations which therefore similarly collect this gas.

It is this concept of thin pockets of gas under high pressure throughout the planar openings within a grain which has been designated as the planar-pressure theory of hydrogen embrittlement,^{58,60} the embrittlement resulting from systematic immobilization by aerostatic distortion of the internal surfaces active in slip.

Experimental.

Specimens Deformed Before Charging.

By coating the surface of iron with oil or Canada balsam, the escape of hydrogen can be made visible. A $\frac{1}{2}$ -in. block of 4.24% silicon ferrite (prepared for another research⁵⁶) was polished, deformed in a vice, cathodized in a 10% NaOH solution at 1 amp./sq. in. for 90 min., coated with balsam, and studied under the microscope with an oil-immersion lens.

Cathodizing severely etched the specimen, but the Neumann bands were still clearly visible. By keeping the focus on as many bands as possible at such high magnification, bubbles were soon observed appearing with fair regularity. Heating the back of the specimen with a soldering iron greatly accelerated the effusion.

In every case, bubbles issued only from a Neumann band or from some other visible surface

orifice. Furthermore, each bubble burst suddenly into view, attaining instantly a common size and exhibiting no further growth.

These observations are of the greatest importance, and they afford virtual proof for planar occlusion within the Neumann band. There was never evidence of a bubble nucleus appearing and gradually growing to size, which process would conform with a concept of lattice diffusion and evaporation; nor did a bubble ever appear that did not issue directly from a deformation marking. The appearance was exactly that of a gas pocket from which a quantity of gas suddenly issues by a blow-off valve; and it is in exact conformity with the planar-pressure theory of hydrogen embrittlement.^{53,60}

In Fig. 12, which is a photomicrograph of a silicon ferrite sample, a bubble is shown which issued from the intersection of a Neumann band with a visibly fractured inclusion. The cathodic etch should be noted, and also what appears to be a resistance of the bands to etching. This differential etching is better shown in the photomicrograph of Fig. 13 taken at lower magnification. Its cause is not known to the author, and these observations of the phenomenon are submitted as incidental data remaining to be explained. The photomicrograph in Fig. 14 is included to show that the specimen contains a precipitating phase, apparently of the Widmanstätten type. While such phases are known to be nucleated by deformation, it is beyond the scope of this paper to suggest a relationship with the unattacked bands in Fig. 13. The answer may be associated instead with the electropositeness of the strained bands with respect to the matrix.

Another incidental observation is shown in Fig. 15, where the edge of the balsam film may be seen to wet the Neumann bands far in advance of the remainder of the specimen. The considerably increased surface energy indicated by that action may stand as evidence in favour of the shearing theory for Neumann bands because of the fresh surface presumably exposed.

Specimen Deformed After Charging.

The foregoing experiment indicates that the Neumann band contains actual physical openings which collect hydrogen during and/or subsequent to charging. While this condition is consistent with the evidence cited from the literature, and also with that contained in such fractographs as Fig. 11, there is no proof that either these hiatuses or the band itself are founded upon an inherent mosaic imperfection.

Consequently, several undeformed specimens were roughly polished and cathodized, then re-polished and etched, coated with balsam, and finally deformed by pressure in a vice. An instantaneous burst of bubbles is observed in such

an experiment which cannot possibly be explained on the basis of lattice diffusion of atomic hydrogen, because the known diffusion rates lack the observed rate of bubble formation by a factor at least in the millions. The evolution of bubbles then virtually stops completely except for a low escape rate corresponding to the degree of charging and the remaining quantity of gas. Once again all bubbles were seen to issue from surface traces of deformation markings which were at least microscopically visible; and the Neumann band proved to be by far the most active source.

The photographing of these bubbles is difficult because of their mobility in the oil. To capture one before it drifted from the orifice a lower magnification was used (Fig. 16), in spite of the entirely unattractive results from photographing through a film of oil with a non-contact lens. In the photographs in Fig. 16, however, several bubbles can be observed just after issuing from a Neumann band.

The importance of this test can scarcely be overestimated, as it proves the pre-existence of the mosaic hiatus; it affords direct evidence for the planar-pressure theory of hydrogen embrittlement; and it demonstrates that *Neumann bands originate in planar defection, that their development involves mosaic structure, and that their location is predetermined on a mosaic scale by the internal surface pre-existent within the grain.*

To explore this phenomenon further, specimens of Armco iron were similarly treated. The photographs in Fig. 17 illustrate essentially the same results that were observed with silicon ferrite. Here, however, slip was a more prominent deformation marking unless the specimen was deformed with suddenness. In every case the bubbles issued from a visible surface trace of a deformation plane, whether Neumann band or slip.

This observation has the metallurgical importance of showing that *slip similarly involves the intragranular surface of the mosaic structure*, whereupon the classical picture of slip as homogeneous atomic shear becomes effete.

It is interesting to note here that Pfeil³⁰ observed that the hydrogen embrittlement resulting from pickling in H_2SO_4 caused a much more prolific development of Neumann bands in a specimen when it was subsequently deformed. The interdependent rôles of hydrogen embrittlement, planar defection, and deformation now lend explanation to Pfeil's observation.

In closing, attention might be drawn to the staining or etching evident beneath several of the bubbles. It is particularly apparent around the bubble in Fig. 17(c); and certain of the peculiar spots in the other photographs of Fig. 17 indicate the former location of bubbles which escaped before photographing. Whether the nascent gas

hydrogenates or acidifies the oil, which then attacks the metal, is not known.

CONCLUSIONS.

The results of this research can be enumerated as follows :

(1) A re-evaluation of the literature on Neumann bands shows that :

(a) There are established cases in which the phenomenon involves twinning.

(b) There seem to be established cases in which the phenomenon does not involve twinning.

(c) In all cases it is agreed that a great deal of disorganization exists in the matrix surrounding the band.

(2) From these conclusions a new theory for Neumann bands is developed which states that the Neumann band is primarily a shearing or faulting movement operating along the pre-existent planar disjunctions of the mosaic structure, and that as a secondary operation twinning may be completed, as is known to be possible in ferrite. This twinning has a probability varying from nearly 1.0 in bismuth, tin, zinc, and such metals known to deform by twinning, to nearly zero in certain other metals where deformation is known not to produce twins. For ferrite, the probability is intermediate, and twins may or may not be formed. The occurrence of twinning is not fundamental to the argument.

(3) Fractographic study of Neumann bands in ingot iron and silicon ferrite, while not disallowing twinning, strongly corroborates the present theory by revealing apparent shear surfaces on nascent crystallographic facets, by allowing observation of several deformation phenomena which are interdependent with the bands, and by providing direct evidence of a marked imperfection structure.

(4) Hydrogen diffused into previously deformed metal and subsequently captured under an oil film as it escaped, proves the presence of real physical hiatuses within the band by the fact that the gas appears suddenly as bubbles of discrete and regular size and that they issue only from Neumann bands or other visible surface orifices. They do not grow visibly after formation, as would be expected if lattice diffusion were playing a significant part.

(5) By charging a specimen with hydrogen and subsequently deforming it under oil, a flush of similar bubbles immediately develops, and again they issue only from deformation markings. When ingot iron is used instead of silicon ferrite, bubbles can be seen to issue from slip markings also, thereby proving that slip, too, originates within mosaic structure and not according to the classical concept of homogeneous shear.

(6) These phenomena of gas diffusion, occlusion,

and liberation demonstrate and prove the planar-pressure theory for hydrogen embrittlement, the presence of mosaic structure, and the dependence of deformation and slip upon an intrinsic mosaic system of planar defections which transcend mere lattice distortion.

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CORRESPONDENCE.

(Fig. A = Plate XIII A.)

Professor G. CHAUDRON (Paris) wrote: We have read with great interest Dr. Zapffe's paper on Neumann bands and the theory of hydrogen embrittlement. We have in particular admired the micrographs in which the author shows the issuing of hydrogen bubbles from Neumann bands.

We would refer in this connection to our own investigations on a closely related subject, the results of which were published during the last few years.* If a polycrystal is electrically charged with hydrogen it is possible to observe in cedar oil the evolution of hydrogen bubbles on the grain surfaces. In the case of a single crystal we showed that it is possible to subdivide the crystal into small crystallites of the order of 10^{-4} cm. This sub-structure is visible in an ordinary microscope

at a magnification of about $\times 2000$. A banded structure is observed (see Fig. A), which becomes the clearer the more prolonged the loading with hydrogen has been.† Along these bands the issue of hydrogen, which is effused in the cedar oil, can be observed. The orientation of this sub-structure is obviously governed by that of the surface. These micrographic results were confirmed by X-ray examinations.

This leads to the conclusion that the path of atomic hydrogen through an iron crystal produces a modification of its structure which is quite analogous to that observed in the case of mechanical cold-hardening. A single crystal is transformed into a sort of fibre, the hydrogen causing in fact a rotation of the crystallites of the mosaic

* G. Chaudron, *Revue de Métaux et Corrosion*, 1944, Sept.-Oct., p. 92.

† G. Chaudron and L. Moreau, *Comptes Rendus*, 1944, vol. 219, Aug. 16, p. 26.

structure. When studied by X-rays, the single crystal which gave originally a Laue diagram exhibits an oriented Debye-Scherrer diagram. This leads to hardening of the metal. The evolution of hydrogen at room temperature, which can be obtained by ionic bombardment, according to Chaudron and Moreau,* does not affect the work-

hardening structure of the metal, and consequently does not modify its hardness.

Finally, our experiments show that the hydrogen in supersaturated solution in the lattice tends to evolve through all defects of the structure, such as inclusions, intergranular spaces, intermosaic spaces, slip bands, Neumann bands, &c.

AUTHOR'S REPLY.

The AUTHOR wrote in reply: Professor Chaudron's remarks are much prized, for a half-dozen papers under the authorships of Chaudron, Moreau, and Portevin have recently come to our attention which agree in detail with our own observations. Since there has been a marked

resistance in America to the concept of mosaic structure, and consequently to the planar-pressure concept of hydrogen embrittlement, it is most reassuring to have this verification from renowned French investigators.

* L. Moreau, G. Chaudron, and A. Portevin, *Comptes Rendus*, 1935, vol. 201, July 16, p. 212.



FIG. A.—Single-Crystal Sample of Armco Iron, charged by electrolysis with hydrogen for 12 hr. at -10°C. , at 5 amp./sq. dm. The white zones are due to the liberation of hydrogen in the cedar oil. (See G. Chaudron's contribution.)

[Correspondence on Zapffe: Neumann Bands.

[To face p. 132 P.



FIG. 1.—Cast-Iron Spectrograph Sample, with identification label.

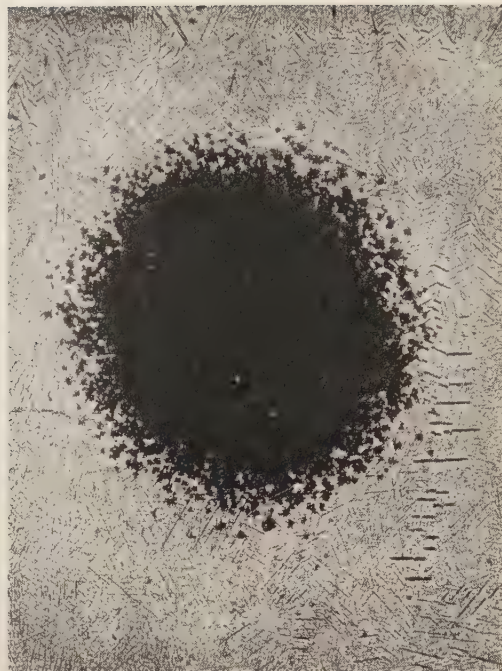


FIG. 2.—Spark Area Superimposed on Microstructure of Ingot-Type Sample. $\times 12$.



FIG. 3.—Rotary Cutting Tool for Forming Electrode Tip.

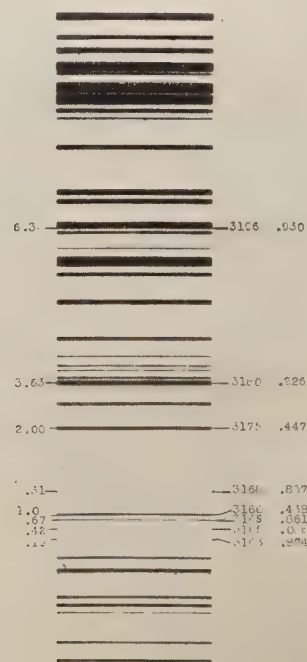


FIG. 4.—Relative Intensities and Wavelengths of Calibration Lines.

[Hurst and Riley.
[To face p. 133 P.

ROUTINE SPECTROGRAPHIC ANALYSIS OF CAST IRON.*

By J. E. HURST, D.MET., AND R. V. RILEY, PH.D. (THE STAVELEY/BRADLEY-FOSTER RESEARCH DEPARTMENT, DARLASTON).

(Figs. 1 to 4 = Plate XIV.)

SYNOPSIS.

A method for the routine spectrographic analysis of cast iron, which has been used for over a year, is described. The spectrographic technique is found to be ideal for the rapid and accurate analysis of a variety of plain and alloy cast irons for all elements except carbon, sulphur, and phosphorus. The method in use, with modifications, is similar to the flat-surface technique recommended by Barker for steel. The importance of suitable layout of the laboratory, representative analytical samples, and rigid standardization of procedure in the attainment of accuracy in routine analysis, is stressed. The single- and multi-spot methods of sparking are compared, and the considerations affecting the choice of excitation, and the influence of air blast at the analysis gap on the duplication of the results, are dealt with. Details are given of a method of plate calibration based upon the relative intensities of a group of standard lines in the iron spectrum; the method has enabled a complete analysis of all major metals normally present in cast iron to be estimated accurately from one exposure. Standard chemically analysed samples are used only for the establishment of "working graphs" from which the percentages of alloying elements in routine samples are read.

INTRODUCTION.

PHYSICAL methods of chemical analysis, of which the spectrographic method is a prime example, are finding increasing favour in the modern metallurgical analytical laboratory. For routine estimations such methods can claim certain advantages over the orthodox chemical operations. The spectrographic method, in particular, can claim the advantage of being more readily standardized in details of procedure and of being easily split up into simple elemental operations which may then be carried out by junior staff with more precision than many of the well-known chemical methods. The saving in time and economy in chemicals are points also strongly in favour of spectrographic methods. With the advent of closer specification limits, and hence the need for a correspondingly greater number of check analyses to control metallurgical operations, this disparity in costs between the two methods is further increased in favour of the spectrographic method.

The spectrographic equipment and method have now been in operation in the authors' laboratory for over a year, and have been applied exclusively to the routine analysis of cast iron with complete success. Although in America the spectrograph has been applied for this purpose, in England, so

far as the authors were able to ascertain at the time their installation was made, the apparatus had not been used in the regular routine analysis of cast-iron alloys. The successful adaptation of the spectrograph to the determination of constituents in cast iron has involved considerable development work, and for these reasons it was felt that a full description of the methods evolved would be of value to those interested in metallurgical analysis, particularly the analysis of cast iron.

In addition to the routine analysis of refined pig-iron samples, bath samples from electric furnaces in a foundry manufacturing heat-, acid-, and wear-resisting castings, and samples of a variety of incoming raw materials, are dealt with in a routine manner. At present the average number of samples analysed weekly varies between 100 and 150, *i.e.*, 600 to 900 individual estimations.

The spectrographic method cannot be applied, at the moment, to the analysis of gases in metals, nor, unfortunately, to the estimation of carbon, phosphorus, and sulphur in iron. These elements are determined in the routine chemical laboratories, using the Ströhlein volumetric apparatus for carbon and the high-temperature combustion apparatus for sulphur. Low phosphorus contents are estimated on the Spekker absorptiometer, and high phosphorus contents by chemical methods.

* Received September 3, 1945.

Nitrogen, oxygen, and hydrogen in iron are determined by the vacuum-fusion apparatus. All other determinations are made with the spectrograph. The following types of cast iron are regularly analysed :

Reference No.	Type of Cast Iron.
1	Hematite pig iron.
2	Refined malleable pig irons (white to grey fracture).
3	Refined cylinder iron (low phosphorus).
4	Refined cylinder iron (medium phosphorus).
5	Refined cylinder iron (high phosphorus).
6	Nickel-alloy irons.
7	Nickel-chromium alloy irons.
8	Chromium-alloy irons.
9	Molybdenum-alloy irons.
10	Copper-alloy irons.
11	Heat-resisting irons (Sisal type).
12	Martensitic irons (Ni-hard type).

The range of chemical compositions determined by spectrographic analysis is as follows :

Total carbon *	2.50-4.00%
Silicon	0.35-6.50%
Sulphur *	0.03-0.15%
Phosphorus *	0.05-0.80%
Manganese	0.20-1.50%
Nickel	trace-5.00%
Chromium	trace-3.00%
Copper	trace-2.25%
Molybdenum	trace-2.50%

* These elements are not determined spectrographically.

It is true to say that the bulk of cast irons in normal engineering use may be analysed quantitatively by the spectrographic method. The spectrographic laboratory also examines qualitatively or semi-quantitatively a very large variety of ferrous scrap and raw materials. In this connection the confirmation of the presence or absence of a particular alloying element usually results in a great saving in time. This qualitative and semi-quantitative examination is not confined to ordinary alloying elements, but embraces vanadium, titanium, tin, lead, columbium, cobalt, tungsten, aluminium, and zirconium, for which spectrographic standards are now available in the laboratory. Other rarely occurring elements may be detected by the well-known spectrographic methods, using reference tables of wave-lengths. The spectrograph is also useful for checking the purity of precipitates obtained in the chemical laboratory.

APPARATUS USED AND CONSIDERATIONS GOVERNING THE DESIGN OF THE LABORATORY.

The complexity of the iron spectrum necessitates the use of a spectrograph having a large dispersion, sufficient to ensure adequate resolution of the iron and alloying-element lines. The equipment now in use comprises a Hilger large quartz spectrograph, a Hilger non-recording photo-electric

microphotometer, and a Judd Lewis spectrum comparator. This standard outfit is essentially the same as that in use at the Admiralty Department, Sheffield, which has been fully described by Barker.¹

The general principles of spectrographic technique are now widely understood, and have been adequately treated in the technical press.^{2, 3, 4} But the application of these principles to specific types of metallurgical analysis has not been so satisfactorily worked out, and in evolving the spectrographic technique for alloy cast irons, the authors found it necessary to rely largely upon individual experiments with the particular alloys which it was required to analyse.

The spectrographical laboratory building comprises five rooms, as shown in the detailed plan in Fig. 5 and described below :

Specimen-Preparation Room, containing two grinding machines, and storage cupboards for specimens.

Spectrographic Room, housing the spectrograph and accessory electrical items connected with the arc and spark source.

Dark-Room for Plate Processing.

Calculation Room, housing the microphotometer, Judd Lewis comparator, standard reference plates, graphs, &c., and cupboards for plate storage.

Routine Laboratory Office, shared by the adjoining chemical laboratory to house laboratory records and to serve as headquarters for the metallurgist-in-charge and the senior chemist and spectroscopist.

Each room in the laboratory is separately thermostatically controlled and a steady temperature is maintained by electric low-temperature tubular heaters working in conjunction with a general scheme of central heating for the whole building. Special care was taken in siting the dark-room to obtain constant-temperature conditions. As it is completely surrounded by other rooms or internal corridors, its walls are not subject to fluctuating temperatures, and the atmospheric temperature is arranged to remain constant at $67^{\circ} \pm 1^{\circ}$ F.

The amount of electrical power consumed by the complete spectrographic outfit is small, and the spark generator itself is rated at $\frac{1}{4}$ kVA. The laboratory was, however, purposely wired with oversize cables, so as to avoid, as far as possible, a drop in voltage due to line resistance when current is taken from the mains. The supply to the laboratory is taken direct from the works sub-station. In this way a remarkably steady mains voltage at the primary of the 15,000-V. transformer is secured, which is almost completely unaffected by variations in electrical load inside and outside the laboratory.

The hardness of the water in South Staffordshire necessitated the fitting of a Permutit water-softener to the water main used for supplying

cloudy, thereby eliminating a source of error in the spectrographic method.

Variable conditions of humidity in the labora-

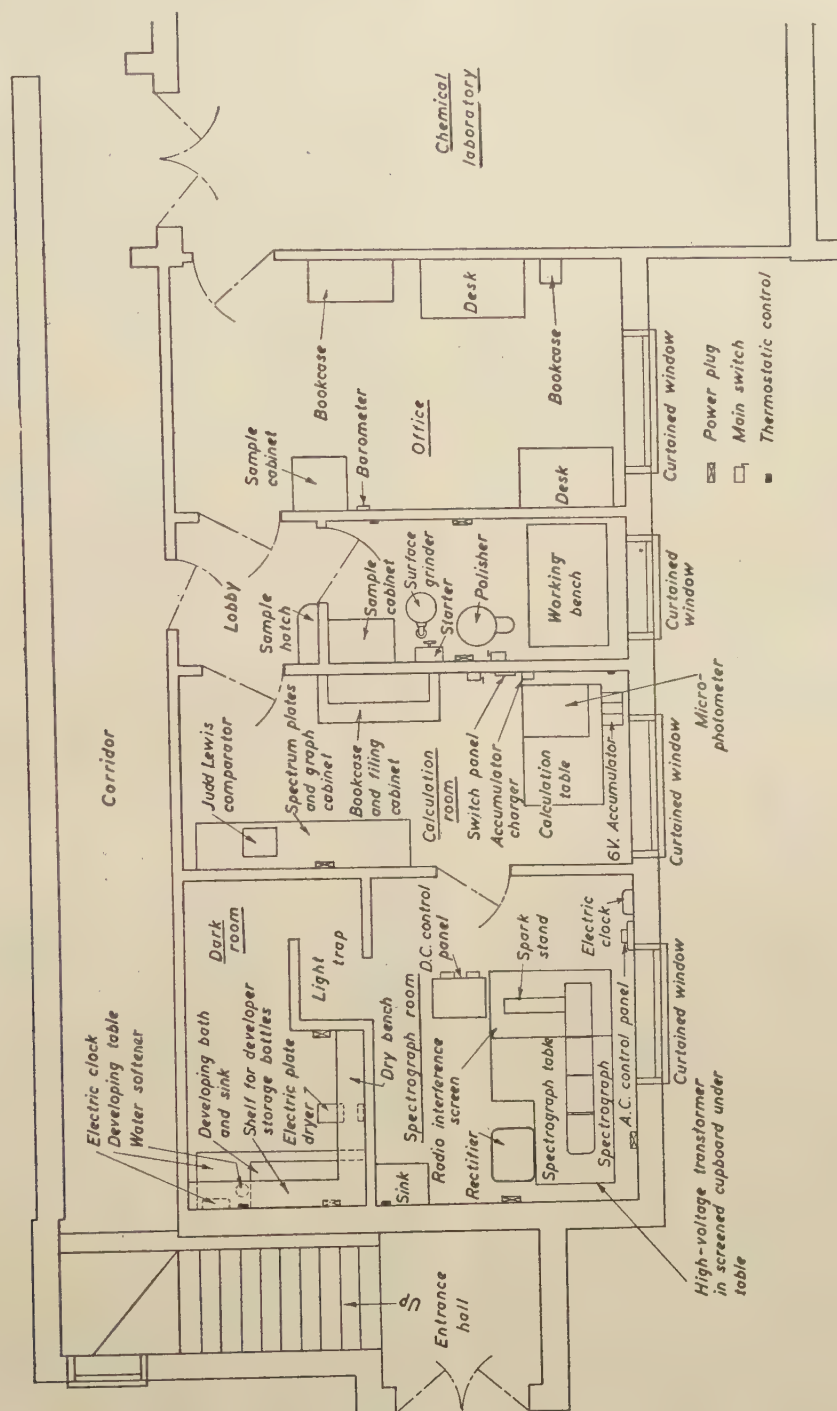


FIG. 5.—Plan of Spectrographic Laboratory.

plate-washing water in the dark-room. The use of softened water for this purpose prevents the photographic emulsion from absorbing small particles of calcium or magnesium salts and becoming

tory atmosphere such as normally occur in the district have not been found to have any important effect upon the reproducibility of the results of spectrographic analysis. It was not considered

essential, therefore, to condition the air in the laboratory, although this would be an advantage from the point of view of dust elimination.

THE SAMPLING OF CAST IRON FOR SPECTROGRAPHIC ANALYSIS.

The taking of a sample for analysis is a major consideration in ensuring accuracy. The minute amount of volatilized metal consumed in the spark gap during an exposure (about 1 mg.) is much less than that used in the average chemical estimation, so that extra care must be taken in spectrographic analysis to obtain a homogeneous, truly representative sample of the metal under test. Early investigations on the spectrographic analysis of cast iron, using sand-cast samples, gave very disappointing results. Discrepancies in analysis were shown to be due to heterogeneity in the sample, and little headway was made with the

coarse graphite. The grain-size of the metal is relatively small in comparison with the area covered by the spark, which is shown superimposed on the microstructure in Fig. 2. Because of the small grain-size of the sample, little difficulty has been experienced from heterogeneity, which can result in a tendency to preferential sparking. The successful employment of the spectrographic method with cast iron is largely dependent upon the adoption of a chill-cast sample.

Table I. shows an interesting comparison between the time involved in sampling a 10-ton cast of refined iron for the spectrograph and the time required to obtain a sample for chemical analysis. It is clear from the table that the spectrographic method effects a considerable saving of time in the sampling operation and, in addition, the method can also claim the advantage of being less likely to result in the contamination of the sample. The ingot sample for spectrographic analysis is permanent and may be easily stored against future requirements; whereas it is seldom convenient to packet sufficient drillings to meet all possible rechecking demands, and consequently it is usually necessary to hold in stock bulky pieces of pig iron. The laboratory normally stores spectrographic samples of refined iron casts for three weeks, in partitioned trays in a wooden cabinet. After this period the samples are discarded unless specially required. The laboratory has, of course, a permanent record of the samples in the form of the exposed spectrographic plates. These are stored indefinitely in boxes of twelve in partitioned drawers.

With the fine-grained chill-cast samples it is necessary to spark the sample in only one spot to secure a spectrum truly representative of the iron. In the initial work with coarse-grained or graphitic irons a single point of sparking was found to be insufficient, and as many as six spots were sparked and the spectra superimposed to obtain a more correct representation of the sample. This method was time-consuming and the results contained in Table II. demonstrate that multi-spot sparking with chill-cast irons is not only unnecessary, but is not so conducive to accuracy as is the single-spark method. With chill-cast samples of standard type, therefore, the single-spot sparking method has been adopted.

The laboratory occasionally undertakes analytical work on samples of a non-uniform type, and accurate results may be obtained using the standard methods described in this paper provided that the samples are not of coarse grain or grossly heterogeneous. Caution is necessary in reporting analyses made on non-uniform samples. The results are never relied upon unless previous trials with similar material have shown the spectrographic estimations to be in agreement with those of chemical analysis.

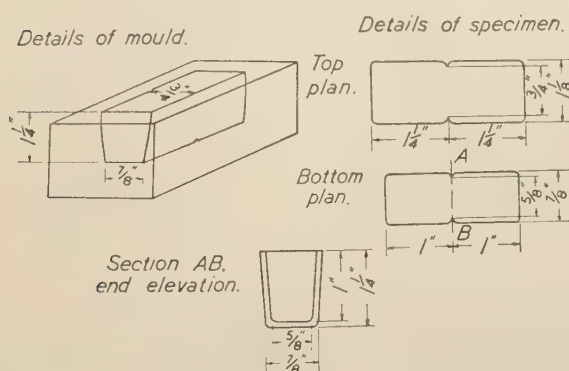


FIG. 6.—Details of Mould and Specimen.

spectrographic method until homogeneous, fine-grained samples were produced by chill casting.

The form of sample finally adopted was a small chill-cast ingot, roughly $2 \times 1 \times 1$ in., which is readily cast in a chill iron mould having the dimensions given in Fig. 6. The sides of the mould are given sufficient taper to allow the specimen to be readily withdrawn, and its removal is aided by a small loop of 18 S.W.G. soft iron wire cast into the ingot. The wire also serves to form an attachment to which an embossed lead identification label is fastened (Fig. 1). The ingot is then broken at the centre notch by a hammer blow, and the half to which the label is attached is taken to the spectrographic laboratory. The fractured surface of the ingot sample is made flat on a table grinder and is then finish-ground on a No. 1F emery disc. The two grinding operations give a surface of sufficient smoothness for use in the spectrograph and take only 2 min.

The ingot-type specimen is used for all molten-metal sampling, and with all the irons in current production the rate of cooling in the chill mould is sufficiently great to produce a white iron free from

THE SPECTROGRAPHIC METHOD AS APPLIED TO CAST IRON. *Considerations Affecting the Choice of Method of Excitation.*

In the authors' opinion, success with the spectrographic method of analysis of cast iron can be attained only by the rigid standardization of procedure. As in other modern physical methods

(a) *Gap Width and Electrode Characteristics.*

Experiment showed that the high-voltage spark method of excitation was most suitable for the quantitative analysis of irons of the compositions

TABLE I.—*Comparison of Times Required to Obtain Samples for Chemical and Spectrographic Analysis.*

Operation.	Sample for Chemical Analysis.	Elapsed Time, min.	Sample for Spectrographic Analysis.	Elapsed Time, min.
1	Sand-cast pig taken from pig bed after allowing time for slow cooling to ensure an easily drilled sample.	90	Small chill-cast ingots poured at same time as cast of pig iron.	1
2	Pig fractured when cold, cleaned by grinding and wire-brushing.	6	Sample broken in half.	1
3	Pig drilled at five points on fractured surface.	5	Surface of fractured ingot ground on rough and smooth wheels.	2
4	Drillings magnetically cleaned to eliminate sand, and sampled by grinding and sieving. Prepared drillings packed for the laboratory.	3	Surface of ingot washed with alcohol and dried in air blast.	$\frac{1}{2}$
	Total elapsed time, min.	104	Total elapsed time, min.	$4\frac{1}{2}$
	Total operational time, min.	14	Total operational time, min.	$4\frac{1}{2}$

TABLE II.—*Comparison of the Single-Spot and Multi-Spot Methods of Sparking.*

No.	Sparked Once (Normal Method).			Sparked Three Times (using Established Graphs).		
	Individual Silicon Estimation, %.	Error (e), %.	e^2	Individual Silicon Estimation, %.	Error (e), %.	e^2
1	2.09	-0.01	0.0001	2.28	+0.02	0.0004
2	2.11	+0.01	0.0001	2.20	-0.06	0.0036
3	2.11	+0.01	0.0001	2.18	-0.08	0.0064
4	2.10	0.00	0.0000	2.23	-0.03	0.0009
5	2.12	+0.02	0.0004	2.18	-0.08	0.0064
6	2.15	+0.05	0.0025	2.36	+0.10	0.0100
7	2.03	-0.07	0.0049	2.26	0.00	0.0000
8	2.13	+0.03	0.0009	2.34	+0.08	0.0064
9	2.04	-0.06	0.0036	2.32	+0.06	0.0036
10	2.13	+0.03	0.0009	2.25	-0.01	0.0001
	Average silicon content = 2.10%	$\Sigma e^2 = 0.0135$		Average silicon content = 2.26%	$\Sigma e^2 = 0.0378$	
Standard deviation = $\sqrt{\frac{\Sigma e^2}{n-1}}$ = 0.039 or = 1.8% of silicon content.				Standard deviation = $\sqrt{\frac{\Sigma e^2}{n-1}}$ = 0.065 or = 2.9% of silicon content.		

of chemical analysis, it is necessary to adhere very closely to a fixed routine of operations. This demands an operator not having individual skill, as in the case of a well-trained chemist, but one well versed in physical principles and willing to observe strictly the established routine. As much as possible is done to render the processes mechanical and invariable, in order to reduce the risk of avoidable inaccuracies.

already given. The optimum gap width was found by experiment to be 2 mm., and the gap is carefully adjusted to this width before each sample is sparked. An optical-projection method is used to position the upper graphite electrode, and the horizontal flat surface of the ingot sample is then brought up to the sparking position and the gap tested by a feeler gauge. The maintenance of a correctly adjusted gap width is important, since

variations affect the intensity of the spark, which in turn affects the relative intensities of the spectral lines. The graphite electrode is sharpened to an 80° point, so as to concentrate the effect of the spark on to a small area of the sample immediately below the electrode. The concentrated spark thus obtained erodes the point of the graphite electrode and thereby increases the gap width. To reduce this change in gap width during sparking, while preserving the concentrating influence of a point, an electrode tip having a blunted or rounded point is now used (see Fig. 7). The standard form of electrode tip is readily obtained

hoped thereby to obtain more regular sparking and to increase the degree of excitation of the sample, which in turn would result in a greater spectral line intensity. An increase in line intensity was secured, but the frequency of sparking became more irregular. When samples were analysed by this tandem-gap method, the results contained greater experimental errors than those occurring in the simple condensed-spark technique now in use. A blast of air across the auxiliary gap for de-ionization purposes gave no improvement in the results of the tandem-gap method.

An air blast across the analytical gap in the

TABLE III.—*Influence of Air Blast at Analysis Gap on Reproducibility of Results.*

No.	Normal Spark Method.			Air-Blown Analysis Gap (using Established Graphs).		
	Individual Silicon Estimation, %.	Error (e), %.	e^2	Individual Silicon Estimation, %.	Error (e), %.	e^2
1	2.09	−0.01	0.0001	1.97	+0.02	0.0004
2	2.11	−0.01	0.0001	1.96	+0.01	0.0001
3	2.11	−0.01	0.0001	1.96	+0.01	0.0001
4	2.10	0.00	0.0000	1.97	+0.02	0.0004
5	2.12	+0.02	0.0004	1.90	−0.05	0.0025
6	2.15	+0.05	0.0025	1.93	−0.02	0.0004
7	2.03	−0.07	0.0049	1.92	−0.03	0.0009
8	2.13	+0.03	0.0009	1.99	+0.04	0.0016
9	2.04	−0.06	0.0036	1.98	+0.03	0.0009
10	2.13	+0.03	0.0009	1.92	−0.03	0.0009
Average silicon content = 2.10%		$\Sigma e^2 = 0.0135$		Average silicon content = 1.95%		$\Sigma e^2 = 0.0092$
Standard deviation = $\sqrt{\frac{\Sigma e^2}{n-1}}$ = 0.039 or = 1.8% of silicon content.				Standard deviation = $\sqrt{\frac{\Sigma e^2}{n-1}}$ = 0.035 or = 1.8% of silicon content		

with a specially designed rotary cutting tool (Fig. 3), which has been described elsewhere.⁵

(b) Spark Circuit.

A simple condensed-spark circuit working from an A.C., 15,000-V. source, with no added induc-

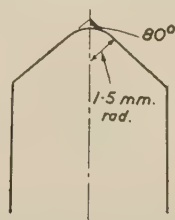


FIG. 7.—Profile of Blunted Graphite Electrode.

tances, has been found to give the best excitation conditions for cast iron. Attempts at obtaining greater control of the sparking conditions have been made by using a 5-mm. auxiliary spark gap in series with the 2-mm. analytical gap, it being

simple condensed-spark circuit (with no auxiliary gap) was the subject of experiment. The results of a series of analyses on the same standard sample, with and without an air blast, showed that no increase in accuracy accrued from the modified technique.

Table III. shows that a set of determinations made with the simple condensed-spark circuit gives results which, when treated statistically, give the same standard deviation as results obtained when an air-blown analytical gap is used. In the results tabulated, the same specimen was employed in each case and the log intensity ratios of the line pairs were read off from the working graph used in the normal routine analysis. The divergence from the standard practice due to the incorporation of the air blast caused the mean percentage of silicon to work out lower than the true percentage, *i.e.*, 1.95 instead of 2.10%. If the whole technique had been restandardized on the air-blown-gap method, the correct result would, of course, have been obtained under these circum-

stances, and the normal spark method would then have shown a high percentage of silicon. The use of a current of air across the analytical gap causes a change, therefore, in the mean silicon content, but does not affect the degree of reproducibility of the results. The only advantage to be gained by using an air blast across the analytical gap was found when analysing small non-standard samples or chippings of metal which have a tendency to overheat during the sparking operation. The use of the air blast in the authors' laboratory is confined to the analysis of such non-standard samples.

The effect on the log-intensity-ratio curve of adding inductance to the simple condensed-spark circuit, is shown in Fig. 8. When the total inductance in the circuit is small, small variations

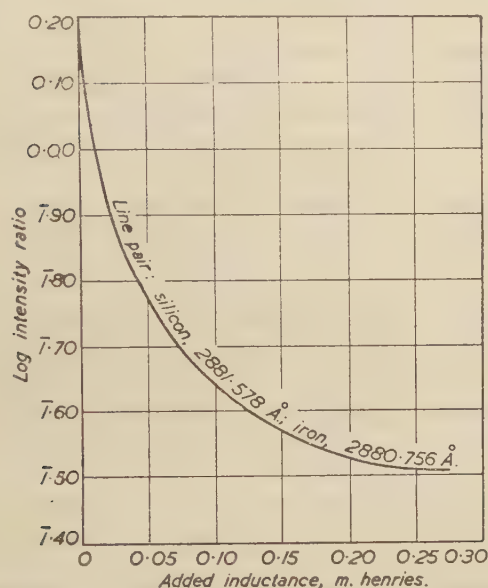


FIG. 8.—Effect on the Log Intensity Ratio of Added Inductance in the Spark Circuit.

in the amount of added inductance have a large effect upon the log intensity ratio of the line pairs and hence upon the estimated percentage of the element concerned. It is desirable, however, in the spectrographic analysis of cast iron to keep the total inductance in the circuit small for several reasons, amongst which are the following:

- (1) To avoid overheating the spark and consequently increasing wear on the graphite electrode, which results in a varying gap width.
- (2) To avoid changing unfavourably the relative line intensities of the line pairs.
- (3) To avoid unduly prolonging the exposure or pre-spark times.
- (4) To avoid a wandering spark which covers too large a spark area.

The curve in Fig. 8 demonstrates the importance of preventing stray or erratic inductance effects

in the wiring of the simple condensed-spark circuit when working at low inductance levels. Stability in the wiring of the spark circuit for the spectrographic analysis of cast iron is essential.

Choice of Spectrographic Plate and Processing Method.

Two photographic emulsions which are most suitable for spectrographic work on irons are the Ilford Ordinary and the Kodak B.10. Both emulsions are supplied on thin glass plates, 2 × 10 in., upon which it is possible to record 15 spectra 2.5 mm. wide, comfortably spaced 0.5 mm. apart. The Ilford Ordinary plate possesses a degree of contrast which is suitable for the range of intensities obtained in the cast-iron spectrum, and is used for most routine work. The Kodak B.10 plate is much more contrasty and is used for irons known to have a composition falling within fairly narrow limits; under these conditions a higher degree of accuracy can be obtained in the analysis. The processing characteristics of the Kodak B.10 are superior to those of the Ilford Ordinary, and the former plate is thus useful for high-speed analysis. The relative operational speeds of the two plates are compared in Table IV. The Kodak

TABLE IV.—Comparison of the Processing Times for Ilford Ordinary and Kodak B.10 Plates.

Operation.	Time for Ilford Ordinary Plate, min.	Time for Kodak B.10 Plate, min.
Developing	2	2
Fixing	2	$\frac{1}{2}$
Washing and dipping in distilled water	10	4
Drying	3	2
Total processing time .	17	$8\frac{1}{2}$

B.10 plate has a finer grain and also shows less background blackening than the Ilford Ordinary plate when fully developed.

Plates entirely from one batch are bought in sufficient quantity to last about the same length of time as the standard developer solution. Re-standardization of procedure is then necessary only at intervals of about two months. Storage of photographic material for this period has no observable effects upon its response or processing characteristics.

The keynote in plate processing, as in other spectrographic procedures, is standardization. The developing, fixing, washing, and drying of the plates are carried out in a scrupulously clean dark-room at constant temperature. The timing of all operations is done to the nearest second, and the routine adopted by the operators is according to a predetermined "drill" to which all must conform. Haphazard plate processing results in uneven

density or mechanical damage to the emulsion, with consequent loss in analytical accuracy. Manual plate processing is in use, and this entails great care on the part of the operator to ensure constant agitation during development. The developer solution is used once only, and is then discarded. A small, controlled amount of a proprietary brand of wetting agent is added to all processing solutions to secure even development and rapid fixing, washing, and drying of the plates. Drying of the spectrographic plates is done speedily with the aid of a hot-air dryer specially made to give the quickest drying time compatible with safety to the emulsion. The solutions used in plate processing are given in Table V.

TABLE V.—*Solutions Used in Plate Processing.*

<i>Developer I.D.2, stock solution.</i>	
Metol	16 g.
Sodium sulphite crystals	1200 g.
Hydroquinone	64 g.
Sodium carbonate crystals	800 g.
Potassium bromide	16 g.
Water up to	8000 c.c.
100 c.c. of stock solution diluted to 200 c.c. with distilled water is used for one plate.	
Development time: 2 min. at 67° F.	
<i>Fixing solution (special rapid acid-hardened hypo).</i>	
Hypo	8 lb.
Sodium sulphite crystals	240 g.
Ammonium chloride	300 g.
Acetic acid glacial	150 c.c.
Potassium alum	240 g.
Water to	16,000 c.c.
Fixing time: Kodak B.10, $\frac{1}{2}$ min. Ilford Ordinary, 2 min.	
<i>Washing water.</i>	
Rapid stream of softened water, followed by a dip in distilled water before drying.	
Washing time: Kodak B.10, 4 min. Ilford Ordinary, 10 min.	

The Line Pairs.

The line pairs suitable for the analysis of iron are, for the most part, those which have been used for the spectrographic analysis of steel. Although the line pairs used are not truly homologous in the strictest spectrographic sense, they have proved to be quite reliable when the whole spectrographic technique is carefully standardized. Table VI. shows the line pairs in regular use for the analysis of refined irons.

The Choice of Standard Spectrographic Samples.

The spectrographic method used in the authors' laboratory involves the preparation of working graphs (described later) from chemically analysed standard samples. The standard samples are in the form of chill-cast ingots of exactly the same type as the samples of refined irons which are

analysed daily in the laboratory. The composition of standard samples is carefully chosen to give, when chill cast, a fine-grained white iron free from graphite, but when sand cast and slowly cooled, a fairly soft iron, easily drilled for chemical analysis. At the same time the standards should, within reasonable limits, have the same iron content and be similar in this respect to the average sample in routine analysis. The variable concentration of alloying elements in iron affects the intensity of the iron line, which, in this spectrographic method, must remain substantially constant. The spectrographic standards must also be chosen with due regard to the relative ease

TABLE VI.—*Line Pairs Used in Spectrographic Analysis of Cast Iron.*

Element.	Range, %.	Wavelength, Å.	
		Element Line.	Iron Line.
Silicon	0.1-0.5	2881.578	2874.172
	0.5-2.0	2881.578	2876.802
	2.0-4.5	2881.578	2880.756
Manganese	0.1-0.6	2933.063	2936.905
	0.6-1.2	3441.988	3443.878
	1.2-1.7	3474.113	3476.704
	1.5-2.0	3474.113	3475.454
Nickel	Up to 1.5	3414.765	3413.135
	1.5-3.0	3515.054	3513.820
	3.0-5.5	3446.300	3443.878
Chromium	Up to 0.4	3593.488	3594.636
	0.4-2.0	3578.687	3586.987
	2.0-3.5	3408.765	3407.461
Copper	0.04-0.5	3273.962	3277.346
Molybdenum	0.05-2.5	2813.154	2816.154
Vanadium	0.05-0.5	3102.299	3100.666
Aluminium	0.10-1.5	3082.155	3083.742
Tungsten *	0.30-1.5	4008.753	4009.717

* Not very sensitive line pair.

with which they may be accurately analysed chemically.

The wide range of percentages which have to be covered spectrographically, necessitates the use of several standard ingots, and the compositions of some of the most useful are given in Table VII. In order to secure a high degree of accuracy over a very small range of percentages, or for other special purposes, a number of sub-standards are in use, consisting of selected samples from routine laboratory operations which are themselves standardized. Such sub-standards are available for some of the rarely occurring elements in cast iron and are very useful in investigational work.

Standard samples are used in the authors'

laboratory for establishing working curves and for the weekly checking of these curves. It is quite unnecessary when employing a standardized spectrographic procedure to spark standard samples along with each batch of routine estimations.

The use of working curves is described fully in a later section dealing with standard routine procedure.

The Calibration of Photographic Plates.

With a carefully standardized spectrographic method it may be confirmed that photographic emulsions bearing the same batch number are remarkably consistent, and analytical errors attributable to plate variations are almost un-

certain limits of intensity. If these limits are exceeded, either in the direction of a stronger or of a weaker source, then the blackening ceases to be directly proportional, and the relationship is governed by what is known as the "gamma" curve of the plate. In the routine spectrographic analysis of iron, the range of compositions to be estimated at the same time is so wide that it is impossible, under standard conditions of excitation, to obtain on the same plate a number of spectra the line pairs of which conform to the limits of intensity imposed by the straight portion of the gamma curve. The use of more than one line pair to cover the whole range of any one element is very helpful and so is the correct choice of plate

TABLE VII.—*The Compositions of Standard Spectrographic Samples.*

Ref. No.	Si, %.	Mn, %.	Ni, %.	Cr, %.	Cu, %.	Mo, %.	V, %.	W, %.	Al, %.
1	4.14	1.47	2.81	0.58	0.79	1.01
2	0.44	1.08	3.44	0.84	0.92	0.80
3	1.52	1.10	1.02	1.08	1.71	0.58
4	3.95	0.73	0.68	0.58	1.17	0.55
5	0.89	0.29	2.01	0.58	1.84	0.48
6	3.39	0.23	1.21	0.20	0.27	0.22
7	2.08	0.55	5.06	0.45	0.46	0.50
8	2.52	0.37	0.24	0.13	0.55	0.67
10	1.12	0.66	...	2.02
11	1.24	0.92	...	2.38
12	1.48	1.27	...	2.73
13	0.43	0.08	0.11	1.53
14	0.71	0.26	0.47	2.64
15	0.89	1.17	0.78	2.97
16	1.44	1.25	1.03	3.13
17	1.55	1.29	1.19	3.33
18	0.12	0.04	...
19	0.53	0.12	...
20	1.92	0.62	0.35	...
21	2.16	0.85	0.62	...
22	2.40	1.30	1.02	...
23	5.52	1.49	...	2.73	...	1.25	0.05	...	0.05
24	4.84	1.54	...	2.41	...	1.49	0.40	...	0.12
25	4.70	1.62	...	2.59	...	1.67	0.50	...	0.8
26	5.68	2.58	...	1.97	...	1.99	0.80	...	1.0
27	4.58	2.32	...	2.43	...	2.67	0.90

known. It has been found quite unnecessary, therefore, to calibrate photographic plates individually, as is done in some spectrographic laboratories where processing and other operations are not so rigorously standardized. Plate calibration cannot be ignored, however, and batch calibration is very important in the analysis of a material having a somewhat widely varying alloy content, such as cast iron. The effect of varying alloy content is to cause variations in the intensities of the iron lines, and silicon is the element which does, in a normal iron, give rise to most trouble in this respect.

It is well known that to obtain direct linear proportionality between the logarithm of the true line intensity and the blackness of a recorded image, the light value must be such as to fall within

characteristics and of initial exposure; but despite all expedients it has been found necessary to accept blackening values falling on the non-linear portion of the gamma curve. Some attention to plate calibration, therefore, must be given in any method of spectrographic analysis of alloy cast irons.

Method Adopted for Plate Calibration.

The method finally adopted in the authors' laboratory is one based upon the known relative intensities of a certain group of lines in the arc spectrum of pure iron. This method of plate calibration, which is similar to one used by Vanselow and Liebig,⁶ is simple and more generally satisfactory than the stepped-sector methods. The group of lines, shown in Table VIII. and Fig.

4, is so chosen as to occupy a part of the spectrum which contains most of the more generally used line pairs. Variations in background intensity are thereby reduced to a minimum.

Plate calibration and restandardization of working graphs are carried out whenever a new batch of plates is put into use. Three plates are

TABLE VIII.—*Line Wavelengths and Intensities used in Plate Calibration.*

Wavelength of Iron Line, Å.	Relative Intensity.
3162.229	0.11
3163.874	0.19
3168.857	0.31
3165.006	0.42
3165.861	0.67
3166.438	1.00
3175.447	2.00
3180.226	3.63
3196.930	6.30

selected at random from the batch, and these are used for the preparation of the standard working curves and the calibration graph. The work is arranged so that the spectra of the standard samples occupy the central portion of the plate, and iron arc calibration spectra are included at the top and the bottom. Relevant details of the plate calibration method are as follows:

Spectrographic slit: 0.015×2.50 mm., fixed as in normal working.

Electrodes: upper (positive), pure graphite (80° blunted point), lower (negative), pure iron (45° blunted point).

Length of arc: 4 mm.

Current (D.C.): 5 amp.

Time of exposure: 5 sec.

Method of plate processing: As in normal working.

A very steady, smooth-running arc is obtained with these conditions, and the densities of the spectrum image produced in successive exposures remain constant. Variations from the above standard conditions do not produce important changes in the relative intensities of the calibration lines, which indicates the complete suitability of these lines for this purpose.

When the plates have been exposed, processed, and dried, they are read off carefully on the microphotometer after allowing 15 min. for the mains-charged accumulator and standard-intensity lamp to become steady.

The microphotometer is adjusted to give a full-scale deflection of 50 divisions when the beam of light is passing through the clear portion of the plate near to the group of lines. The density or blackness value of each of the nine standard lines is then read off for each of the iron arc spectra on the plate. The results obtained are averaged, and are plotted against the log of the relative intensity value as given in Table VIII. A graph having the form of an inverted gamma curve is

obtained; a portion of this curve covering all normal blackness values is enlarged and is known as the calibration curve of the plate (Fig. 9). For normal blackness values, as in all routine analyses

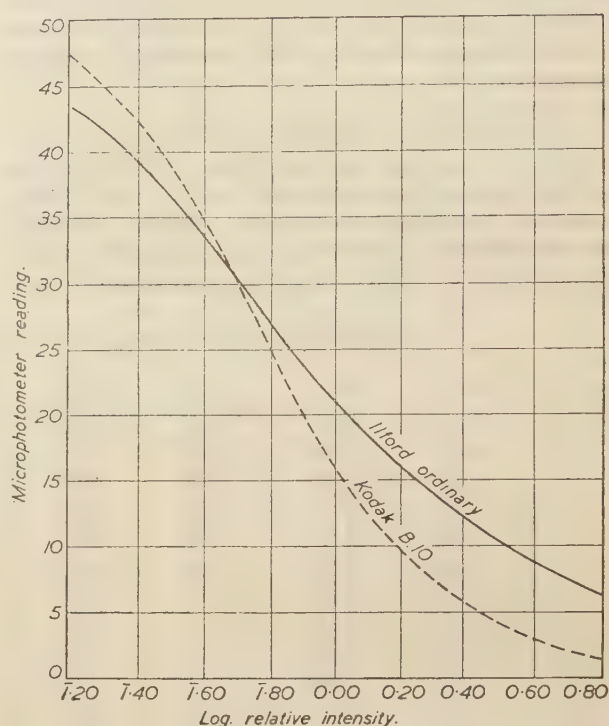


FIG. 9.—Calibration Curves for Spectrographic Plates.

with the exception of those involving very low percentages of nickel, microphotometer galvanometer readings fall within the range 30–8 scale divisions.

THE STANDARD ROUTINE SPECTROGRAPHIC PROCEDURE.

The procedure described for the treatment of routine samples is exactly the same as that adopted for the establishment of the working curves. Great importance is attached to the standardization of the conditions to which the standard samples and the routine samples are subjected. These standard conditions for the treatment of all sparked samples are as follows:

Wave band: 2700–4300 Å.

Width of slit (fixed): 0.015 mm.

Spark gap: 2 mm.

Voltage applied on open circuit: 15,000 V.

Added inductance: Nil.

Capacity: 0.005 μ F.

Upper electrode: Pure graphite (80° blunted point).

Lower electrode: Sample ingot, ground flat.

Pre-sparking time: 25 sec.

Method of plate processing: Standard, as given in Table V.

The processed plate (2 in. wide) containing up to fifteen spectra is read off on the microphoto-

meter. The microphotometer standard settings are:

Micrometer slit: 0.15 mm.
Length of line used: 1.5 mm.
Full deflection: 50 scale divisions.

Special precautions regarding its use include:

(a) Correct focusing of all areas of the plate examined.

(b) A steady rate of operation of the slow-motion device to ensure sufficient time for full galvanometer response.

(c) Correct setting of the photo-electric-cell sensitivity to give a reading of 50 scale divisions on a clear part of the plate near to the line pairs.

Galvanometer-deflection readings, representing line density or blackness values, are taken on the line pairs. The densities of the iron and alloy lines are then read off for all the spectra on the plate and the readings are recorded on working sheets. When one set of line pairs has been read in this way, the plate is moved into position for the next set and the process is repeated.

The galvanometer readings of line density recorded on the working sheets are converted to relative line intensities by reference to the calibration curves of the plate. The relative-intensity axis on this calibration graph (Fig. 9) is plotted logarithmically, and it is then a simple operation to subtract the log relative intensity of the alloying-element line from the log relative intensity of the iron line and thereby to obtain a corrected log ratio of the true line intensities. This true log intensity ratio is then related to the percentage of alloying element by reference to a working curve which has previously been established from spectrographic readings made in exactly the same way upon standard samples.

Typical working curves for silicon in iron are shown in Fig. 10. To maintain accuracy in spectrographic analysis it is necessary to ensure that the alloy-element line and the iron line with which it is compared, are of similar intensity. This means that values for the percentage of alloying element corresponding to a corrected log ratio of 0.00 may be determined with the greatest accuracy. In order to secure optimum accuracy with cast iron which may contain a widely varying alloy content, a number of line pairs are employed, and hence a correspondingly large number of working graphs are needed, of which those shown in Fig. 10 for silicon are typical. Only in exceptional cases is it desirable to work with log ratios outside the range $\bar{I}.70$ –0.30.

Much of the calculation in the spectrographic method outlined here may be avoided by using a specially designed calculating board such as is shown in Fig. 11. Engraved celluloid scales prepared from the working curves are mounted in a

suitable slide over a sheet of graph paper on which is drawn the current calibration curve. The scale is movable in horizontal and vertical directions and may be operated to give the corrected log ratio; or, if special scales are prepared, the percentage of the element directly from the galvanometer readings for the line pairs. Whichever method is used, the galvanometer readings for the apparent intensities are always

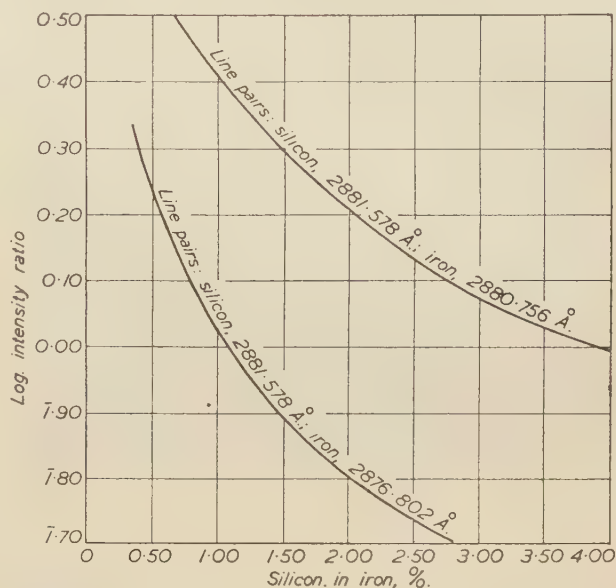


FIG. 10.—Typical Working Curves for Determination of Silicon in Iron.

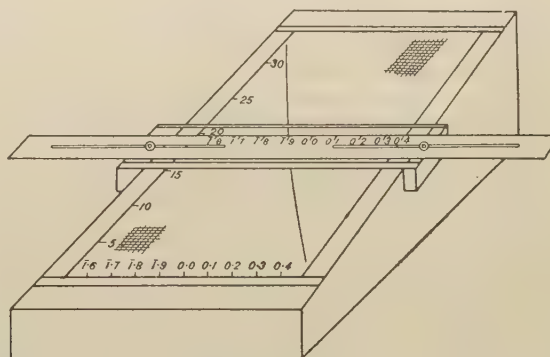


FIG. 11.—Graphical Plate Calculator to take graph paper 10 × 15 in.

entered on the working sheet for future reference and checking. Without this precaution mechanical calculators are liable to be misused, and there is the possibility of introducing serious errors.

THE ACCURACY OF THE SPECTROGRAPHIC METHOD OF ANALYSIS.

The standardized procedure described here is capable under routine conditions of giving an

accuracy of better than $\pm 2.5\%$ of the content of the element being determined. This degree of accuracy is considered adequate for the class of work analysed, and experience with both the chemical and the spectrographic methods indicates that for routine analysis of alloy irons $\pm 2.5\%$ is as good as can be normally expected from either method. The laboratory has, wherever practicable, adopted a practice of doing all routine analyses in duplicate and, if possible, on separate samples. The spectrographic method is particularly adaptable to this method of working. In the case of cupola casts of refined iron, for instance, two samples are taken from each ladle of metal; the first spectrographic sample is taken at the beginning of the casting operation, and the second near the end of casting. The first or *A* samples in every cast are kept separate from all the second or *B* samples. All the *A* samples over a given period are analysed on the same spectrographic plate, whilst all the *B* samples are sparked about 2 hr. later on another plate by a different operator. In this way checks are obtained upon the sampling errors, spectrographic technique, and other unpredictable irregularities. The analytical results from *A* and *B* samples should agree to within

$\pm 2.5\%$. If larger errors than this occur the spectrographic samples are re-sparked, and a chemical check is run on the drillings from a piece of pig.

ACKNOWLEDGMENT.

The authors wish to record their appreciation of the advice and assistance of Mr. F. G. Barker of the Bragg Laboratory, Mr. J. Arnott of Messrs. G. and J. Weir, Ltd., and their staffs in the early stages of the development work.

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CORRESPONDENCE.

Mr. K. M. BILLS (The Mond Nickel Co., Ltd., Birmingham) wrote : The authors are to be congratulated on a paper which should do much to further the use of the spectrograph in the cast-iron industry. It is indeed surprising that such an attractive means of analysis should have been so little used in this country when, as demonstrated by the authors, it is to be recommended if only on the basis of economy and speed. The consistency of the results under the conditions described appears even more excellent when account is taken of the more complicated excitation sources advocated elsewhere to achieve often lower accuracies. The fact that a standard deviation of less than 2% of the content may be obtained using a simple uncontrolled spark-source demonstrates that the electrical conditions in the discharge are by no means the only factor determining the reproducibility of the spectra. It is probable that in many cases the emission is greatly influenced by the resistance to oxidation of the sample under test. This is doubtless the explanation of the effect of silicon in decreasing the total intensity of the spectra, as recorded by the authors, owing to the formation of a tenacious silica layer resistant to the attack of the discharge.

It has been noted that although similar standard deviations are obtained with both the normal procedure and with the addition of an air blast on the analysis gap, the use of the latter has effected a considerable decrease (3.35 to 2.56%) in the maximum deviation from the mean content—a very important factor in the production of material to close specifications. This is probably due to the more steady discharge of a higher potential as observed by Convey and Oldfield,* which, combined with the cooling effect of the air blast, suppresses highly localized selective heating. This is evident in the more closely grouped values of apparently lower silicon content, brought about by a decrease in the emission of Si I. 2881.578 and an increase in the iron line with which it is compared. (It is suggested that Fe II. 2880.756 is the internal standard used and not Fe II. 2876.802, the line tabulated, which is more suitable for the estimation of lower contents, as seen from the typical working curves.) However, the added-inductance/intensity-ratio curve indicates that the estimation of silicon is likely to be most improved by the air blast, as the other line pairs given are not affected in such a degree by varying conditions.

* J. Convey and J. H. Oldfield, *Journal of The Iron and Steel Institute*, 1945, No. II., p. 473 p.

Mr. E. VAN SOMEREN (Murex Welding Processes, Ltd., Waltham Cross, Herts.) wrote: The high standard of precision obtained in this work makes it possible to discuss only points of detail of the method, and these are connected with the Tables and photographic factors.

Table II.—The probable range of error of a standard deviation based on only ten measurements is relatively large, and amounts to about 0.02 on 0.039 and to 0.03 on 0.065; consequently it is not quite safe to claim a definite superiority for the single-sparking method.

Table VIII.—How were the relative intensities quoted here obtained? The writer, who uses the same method of plate calibration, uses one of the same lines and has measured others; the relative intensity of 3165.9 and 3166.4 he finds as quoted, but he finds the relative intensity of 3175.4 to be 2.3 instead of 2.0.

Table V.—The short development time accentuates the soft quality of Ilford Ordinary plates and gives a contrast factor of 0.6 if the data of Fig. 9 are plotted on a density basis. The writer finds a contrast factor of 0.8 more convenient on these plates.

Choice of Plate.—The higher accuracy obtainable in analysis when a more contrasty plate is used is largely illusory, unless the microphotometric measurements are the chief source of error. Here

the total error is so small that the microphotometric measurements must have been good.

From a single series of spark spectra of wrought stainless-steel bar the following measurements were taken in order to estimate the error of manganese determinations at two different values of contrast factor:

Line Pair.		Standard Deviation of Line Density Difference = Δ .	$\frac{d\Delta}{d \log p}$.	Standard Deviation of % Mn = p .
Mn.	Fe.			
2933	2937	0.023	0.91	0.068
4033	4005	0.04	1.53	0.07

The slope of the calibration line is $d\Delta/d \log p$, and is proportional to the contrast factor; when this increases, the scatter of the observations of Δ increases in the same proportion, so that the final precision is unaltered. It would be interesting to learn the values of $d\Delta/d \log p$ for elements other than silicon under these conditions. Replotting the data of Fig. 10 we get values of 0.66 for Fe 2880.7 and 0.71 for Fe 2876.8, which suggests that the line densities were measured on a B10 plate. In general $d\Delta/d \log p = n\gamma$, where γ is the contrast factor and n is the exponent of p in the equation $I = kp^n$, connecting the intensity of the radiation due to an element with p , the concentration of that element in the electrode of the arc.

AUTHORS' REPLY.

Dr. HURST and Dr. RILEY wrote in reply: We would like to thank Mr. Bills and Mr. E. van Someren for their interest in our paper. In replying to Mr. Bills we would say that the extent to which the degree of excitation of the spectral emission is governed by the rates of oxidation of constituent elements in the sample is not known at present. Some work on this subject is proceeding in these laboratories and at a later stage it is hoped to make a further publication.

It is difficult to say how far the maximum difference from the mean of a series of analytical results may be regarded as the measure of true accuracy of analysis. The two results selected by Mr. Bills as showing maximum deviations from the mean in Table III. are from a statistical population having a standard deviation naturally lower than this maximum error. We feel justified in drawing conclusions based upon standard deviation values rather than on maximum errors in spot samples. Although we are aware that an air blast at the analytical gap helps in the reduction of errors where appreciable local heating of the specimen takes place, we hold the view that when using the method outlined in the

paper and employing standard-sized samples, errors due to local heating may be regarded as negligible.

We agree with Mr. van Someren that it is unwise to claim superiority of a spectrographic method based upon the results of only ten estimations. Tables II. and III. were included in the text mainly by way of illustration of the statistical methods adopted in the evaluation of the different methods of procedure. The decision to use the single-spot method of working was taken only after several tables of data of the type under discussion had been obtained.

When the method of plate calibration was first put into operation we had no means of checking the relative intensities of the selected iron lines shown in Table VIII.; they were adopted following a successful extended trial of the method suggested in the article by Vanselow and Liebig (*see* reference 6 of the paper). The relative intensity values given in our paper are those which appeared in this article. We have now obtained a stepped neutral filter for the purpose of checking the accuracy of the relative intensities, and so far we have not discovered

any serious discrepancies, but in view of Mr. van Someren's comments we will pay particular attention to line 3175.4.

The two-minute development time was specially chosen to give a contrast factor suitable to accommodate all the line densities normally found in our range of cast irons without having to adopt more than one exposure time, which would, of course, introduce complications into a routine method.

We are glad to have Mr. van Someren's experimental observations on the relative accuracy of working with high and low contrast factors. The close similarity between the overall accuracies of the two methods of working which is revealed by the figures quoted was not obvious in our practice.

We noticed a definite small improvement in the standard of accuracy with Kodak *B10* plates, but we found this emulsion inconvenient for routine use, owing to the limited range of element percentages which could be determined with one set of experimental conditions.

We can assure Mr. van Someren that the working curves for silicon shown in Fig. 10 were in fact plotted from log-ratio values determined when using the Ilford Ordinary plate under the routine conditions exactly as stated in our paper. We have been in touch with this contributor personally concerning this matter, and we would like to express our thanks for his keen interest in our work.

THE STRUCTURE OF TEMPERED MARTENSITE.*

BY DR.-ING. W. J. WRAŻEJ (IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON).

(Figs. 1 to 4 = Plates XV. and XVI.)

SYNOPSIS.

Martensite must be regarded as a solid solution of carbon in α -iron. The 002, 112, and 202 lines on X-ray photographs taken of 0.9% and 1.2% carbon steels distinctly show its tetragonal structure. In a steel of eutectoid composition the ratio of carbon atoms to iron atoms is 1:24, i.e., in martensite of such a composition, one carbon atom belongs to a set of twelve α -iron unit cells, thus causing tetragonal distortion.

X-ray examination of quenched samples tempered at 100° C. for 24 hr. showed that martensite changes on tempering into ferrite and cementite, the latter being precipitated as particles of primary size (multiples of a unit cell) and shape (plates). The tempered material has thus not the structure ascribed to β -martensite, viz., cubic martensite holding cementite in solution.

Owing to the difference between the ferrite and cementite phases in both structure and parameter there will be internal stresses in tempered martensite. These, together with the small particle size, cause the broadening of the lines on the X-ray photographs, as evidenced by calculations.

Martensite can be tempered even at a temperature as low as 100° C., the first stage of troostite being formed.

INTRODUCTION.

THE places available for the accommodation of the carbon atoms in a martensite unit cell have recently been shown by Petch,¹ his findings being confirmed by Lipson and Parker.² All such places must be regarded as the middles of the edges of interpenetrating α -iron unit cells. From a simple calculation it is found that in a eutectoid steel the ratio of carbon atoms to iron atoms is 1:24, so that the martensite structure formed in steel of such a composition should be represented as a set of twelve α -iron unit cells (24 atoms) distorted by one carbon atom.³ This results in the tetragonally distorted unit cell of martensite. Such a single carbon atom is symmetrically placed, since it occupies the centre of an octahedron at the corners of which are the iron atoms.^{3,4} Hence, martensite can be regarded as a comparatively stable metastable phase.

Although it would not be difficult to picture a martensitic structure with less carbon than the eutectoid composition, it is not so easy to imagine a martensite containing more carbon atoms, as in the case of hypereutectoid steel.

There is no longer any doubt that martensite in a carbon steel must be regarded as a solid solution of carbon in α -iron, distinguished by a tetragonal structure. Such martensite is called α -martensite by some authors, to distinguish it from β -martensite, with a cubic structure, which they

assume to exist in quenched steel after tempering at about 100° C. Epstein,⁵ discussing the opinions put forward by various investigators, describes the results obtained by Honda and Nishiyama, who suggested the existence of β -martensite. According to their view, carbon is retained in solid solution also in β -martensite. Epstein shows a diagram⁵ (*loc. cit.*, Fig. 63) representing the change of the lattice parameter (da/a) with the carbon content.

Since a single carbon atom distorts the α -iron unit cell and thus produces the tetragonality of the martensite structure, there is no way in which any other form of carbon, especially Fe_3C , could be accommodated without causing similarly distinctive distortion.

EXPERIMENTAL.

For the determination of the interplanar spacings in a tempered martensite, two plain carbon steels were chosen with 0.89% of carbon and 0.24% of manganese and with 1.20% of carbon and 0.26% of manganese. The samples were quenched from 780° and 930° C. in 15% aqueous sodium chloride solution after holding for 10 min. at these temperatures in a carbon monoxide atmosphere. The micrographs obtained are shown in Fig. 1.

It was found possible to prepare specimens for X-ray examination in the form of 0.5-mm. thick

* Received July 27, 1945.

rods, by cutting very slowly with a carborundum wheel, applying thorough water-cooling. These rods were etched to remove the surface layer, the etchant being made up of 1 vol. of concentrated sulphuric acid plus 1 vol. of concentrated nitric acid plus 2 vol. of water. The X-ray films, taken in a 9-cm. camera using Co $K\alpha$ radiation with an iron filter, are reproduced in Fig. 3 (a) to (d).

gonality, expressed by c/a , varies with the carbon content.

The spacings expressed as $\sin^2 \theta$ for particular lines determined from the films taken in 9-cm. and 19-cm. cameras using Co $K\alpha$ radiation with an iron filter are listed in Table I.

After quenching as described above, the samples were tempered for 24 hr. at 100° C. (in boiling

TABLE I.—Values of $\sin^2 \theta$ of Quenched Carbon-Steel Samples.

Co $K\alpha$ radiation, iron filter. First of values listed was in each case obtained with 19-cm. camera and second with 9-cm. camera.

hkl	Martensite, Calculated for—		Austenite, Calculated for—		0.89% Carbon Steel, Quenched from—		1.20% Carbon Steel, Quenched from—		Variation with 0.1-mm. Change of Reading.
	$a = 2.847 \text{ \AA.}$ $c/a = 1.04.$	$a = 2.846 \text{ \AA.}$ $c/a = 1.05.$	$a = 3.585 \text{ \AA.}$	$a = 3.600 \text{ \AA.}$	780° C.	930° C.	780° C.	980° C.	
111	0.18626	0.18471	0.1888 0.1905	0.1888 0.1898	0.1889 0.1918	0.1882 0.1881	0.00020 0.00040
101	0.18951	0.18789	Overlapped by 111 line				0.00020 0.00040
110	0.19689	0.19703	0.1970 0.1977	0.1967 0.1979	0.1972 0.1979	0.1970 0.1977	0.00020 0.00040
200	0.24835	0.24628	0.2500 0.2507	0.2500 0.2500	0.2498 0.2502	0.2490 0.2490	0.00025 0.00050
002	0.36404	0.35752	0.3670 0.3670	0.3670 ...	0.3672 ...	0.3585 0.3580	0.00026 0.00052
200	0.39388	0.39407	0.3940 0.3952	0.3951 0.3960	0.3940 0.3977	0.3952 0.3955	0.00027 0.00054
220	0.49670	0.49257	0.4994 0.5007	0.4997 0.5003	0.4997 0.5001	0.4975 0.4959	0.00028 0.00056
112	0.56088	0.55440	0.5675 0.5650	0.5651 0.5642	0.5643 0.5644	0.5542 0.5546	0.00028 0.00056
211	0.58322	0.58176	0.5869 0.5886	0.5868 0.5883	0.5860 0.5886	0.5853 0.5854	0.00029 0.00058
311	0.68297	0.67729	0.6841 0.6861	0.6854 0.6836	0.6851 0.6854	0.6789 0.6787	0.00026 0.00052
222	0.74506	0.73886	...	0.7446 0.7453	0.7451 0.7499	0.7408 0.7396	0.00025 0.00050
202	0.75780	0.75751	Very faint			0.7432 0.7513	0.00024 0.00048
220	0.78750	0.78820	0.7805 0.7827	0.7826 0.7834	0.7787 0.7832	0.7846 0.7832	0.00023 0.00046

The austenite lines (face-centred-cubic structure) and martensite lines (tetragonally distorted body-centred-cubic structure) are clearly visible, although the 002 and 112 lines are weaker in the case of 0.89% of carbon. In all films the high-angle reflection lines (310 and 103) are so indistinct that they cannot be evaluated. This fact as well as the broadening and the diffuseness of all lines indicates that martensite must be regarded as a tetragonally distorted cubic structure. The tetra-

gonality, characterizing martensite, disappeared in all cases, as is indicated by the X-ray diagrams reproduced in Fig. 4 (a) to (d). The same result was obtained when tempering a sample of the 1.2% carbon steel for 1 hr. at 150° C. after quenching from 930° C. (Fig. 4 (e)). For comparison an X-ray diagram of electrolytic iron is shown together with those of the tempered samples (Fig. 4 (f)).

Table II. shows that the $\sin^2 \theta$ values of

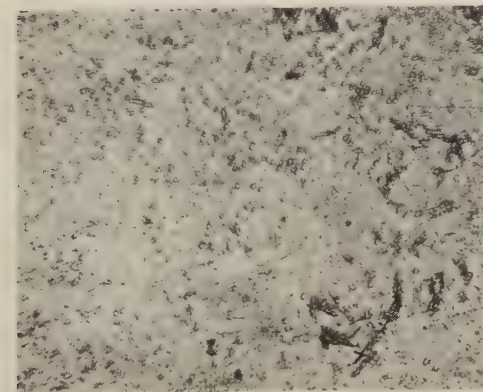


FIG. 1(a).—0.89% Carbon Steel Quenched from 780° C. $\times 400$.

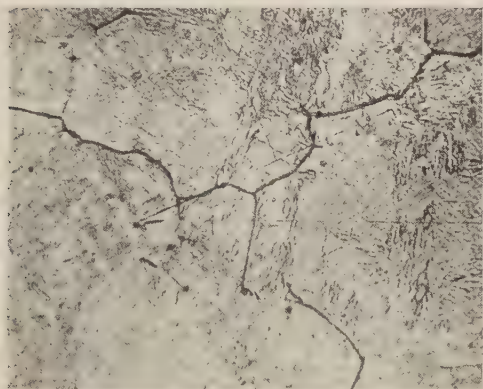


FIG. 1(b).—0.89% Carbon Steel Quenched from 930° C. $\times 300$.

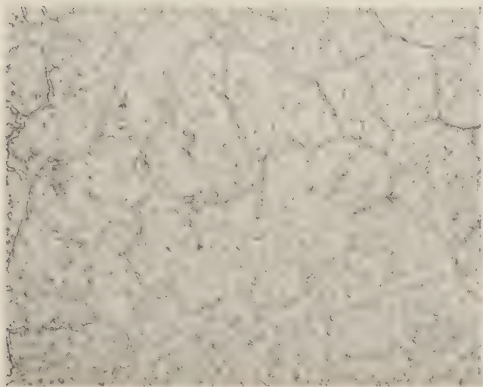


FIG. 1(c).—1.20% Carbon Steel Quenched from 780° C. $\times 400$.

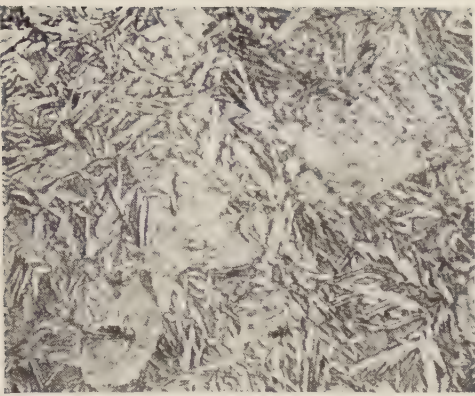


FIG. 1(d).—1.20% Carbon Steel Quenched from 930° C. $\times 400$.



FIG. 2(a).—Sample of Fig. 1(a) after tempering.

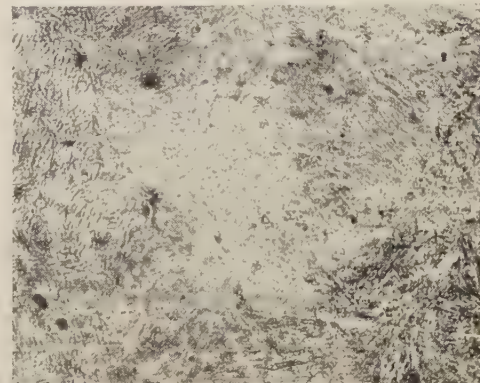


FIG. 2(b).—Sample of Fig. 1(b) after tempering.

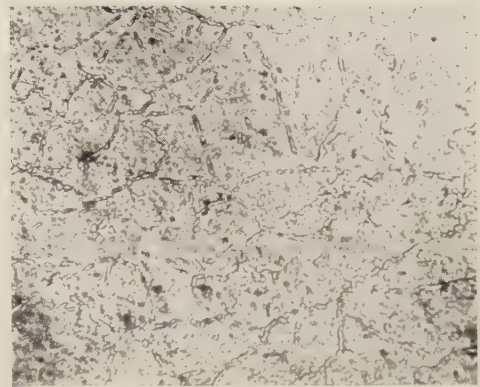


FIG. 2(c).—Sample of Fig. 1(c) after tempering.



FIG. 2(d).—Sample of Fig. 1(d) after tempering.

FIG. 2.—Quenched Carbon Steel Samples Tempered for 24 hr. at 100° C. $\times 400$

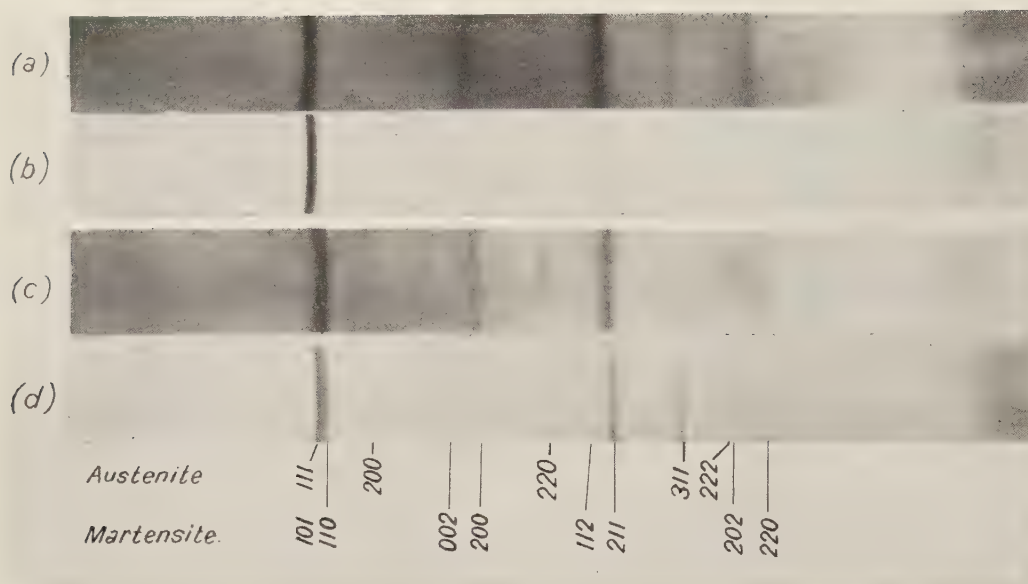


FIG. 3.—X-Ray Films; 9-cm. camera, Co K α radiation, iron filter. (a) and (b) 0.89% carbon steel quenched from 780° and 930° C. respectively. (c) and (d) 1.20% carbon steel quenched from 780° and 930° C. respectively.

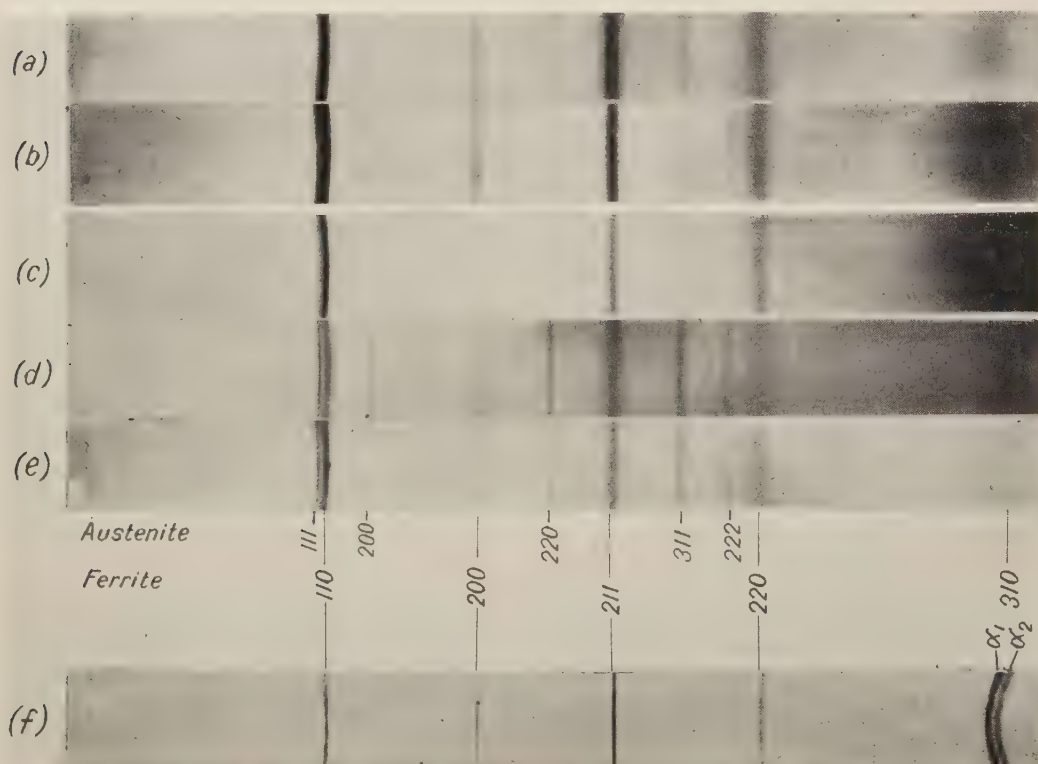


FIG. 4.—X-Ray Films; 9-cm. camera, Co K α radiation, iron filter. (a) and (b) 0.89% carbon steel tempered for 24 hr. at 100° C. after quenching from 780° and 930° C. respectively. (c) and (d) 1.20% carbon steel tempered for 24 hr. at 100° C. after quenching from 780° and 930° C. respectively. (e) 1.20% carbon steel tempered for 1 hr. at 150° C. after quenching from 930° C. (f) Electrolytic iron.

tempered martensite are similar to, and sometimes the same as, those of electrolytic iron. This does not mean that both materials must have exactly the same parameter. As shown by Fig. 4, the difference between the lines of the two substances consists mainly in their breadths. Some of the films taken in the 9-cm. camera were

The microstructures of the tempered samples (100° C. for 24 hr.) are shown in Fig. 2. It was observed that tempered samples could be etched more rapidly (half the time of etching or even less). The micrographs, however, give very little information regarding the change in the microstructure produced by tempering.

TABLE II.—*Values of $\sin^2 \theta$ of Tempered Carbon-Steel Samples.*

Co $K\alpha$ radiation, iron filter. First row of values listed in each case obtained micrometrically from 19-cm. camera film, second row photometrically from 9-cm. camera film, and third row micrometrically from 9-cm. camera film.

hkl	Ferrite, Calculated for $a = 2.8604 \text{ \AA}$.	Electrolytic Iron.	0.89% Carbon Steel Tempered after Quenching from—		1.20% Carbon Steel Tempered after Quenching from—	
			780° C.	930° C.	780° C.	930° C.
111	0.1888	0.1891	0.1892	0.1874
		0.18931
		...	0.1897	0.1897	0.1898	0.1870
110	0.195059	0.1956	0.1963	0.1963	0.1967	0.1962
		0.19578	...	0.1980	...	0.19802
		0.1956	0.1974	0.2021	0.2005	0.1996
200	0.2500	0.2498	0.2500	0.2485
		0.2520	...	0.24880
		...	0.2500	0.2500	0.2505	0.2482
200	0.390118	0.3922	0.3924	0.3927	0.3924	0.3920
		0.39350	...	0.3965	...	0.39413
		0.3911	0.3935	0.3943	0.3943	0.3926
220	0.5003	0.4997	0.4999	0.4950
		0.5032	...	0.49589
		...	0.5004	0.5000	0.4994	0.4948
211	0.584326 (α_1), 0.586881 (α_2)	0.5857 (α_1), 0.5892 (α_2)	0.5857	0.5861	0.5857	0.5861
		0.58736	...	0.5878	...	0.58706
		0.5874	0.5863	0.5883	0.5886	0.5886
311	0.6858	0.6861	0.6849	0.6780
		0.6860	...	0.68046
		...	0.6849	0.6836	0.6844	0.6780
222	0.7465	0.7462	0.7467	0.7389
		0.74373
		...	0.7501	0.7465	0.7484	0.7396
220	0.779101 (α_1), 0.782509 (α_2)	0.7797 (α_1), 0.7834 (α_2)	0.7797	0.7795	0.7791	0.7793
		0.78092 (α_1), 0.78464 (α_2)	...	0.7825	...	0.78127
		0.7800 (α_1), 0.7831 (α_2)	0.7795	0.7802	0.7813	0.7804
310	0.973876 (α_1), 0.978136 (α_2)	0.9740 (α_1), 0.9783 (α_2)	} Very faint and diffuse.			
		0.97416 (α_1), 0.97813 (α_2)				
		0.9740 (α_1), 0.9783 (α_2)				

examined by taking photometer readings along the entire length, the $\sin^2 \theta$ values found in this way being likewise listed in Table II. The similarity of the $\sin^2 \theta$ values indicates that tempered martensite should be regarded rather as ferrite than as a solid solution. The cause of the broadening of the lines of tempered martensite as well as of the slight difference between its $\sin^2 \theta$ values and those of ferrite are discussed below.

DISCUSSION OF THE RESULTS.

The observation that after tempering at low temperatures the martensite lines change over into diffuse ferrite lines may be explained as follows.

In martensite formed in a steel of eutectoid composition (pearlite), one carbon atom distorts a set of twelve iron unit cells.^{3,4} Raising the temperature to, say, 100° C., at which temperature

such martensite can be tempered, enables the artificially retained carbon atoms to escape from their unnatural positions in the α -iron unit cells. It is known that carbon forms cementite of orthorhombic structure,⁶ and that the unit cell of cementite contains four carbon and twelve iron atoms ($4\text{Fe}_3\text{C}$). To form such a unit cell of cementite, neighbouring sets of α -iron unit cells (martensite), must give off their carbon atoms. Since an elementary grain of cementite is built up of multiples of $4\text{Fe}_3\text{C}$, the ferrite block which supplied the carbon must be assumed to be composed of the same multiples of α -iron sets. It may be assumed that particular blocks will be of different size throughout the tempered martensite grain.

The primary cementite may be visualized as layers or plates deposited to a thickness of some multiple of a unit cell along one of the principal planes. Such plates, composed of orthorhombic

and in the parameters, there will be stresses in the grain.⁷ The small particle size of the ferrite as well as the internal stresses due to the distortion of its lattice will cause the broadening of the lines.

The broadening produced by small crystals has been discussed by Jones,⁸ who introduced the conception of the "apparent particle size." This is defined by $\epsilon = \lambda/\beta \cos \theta$, which is independent of the wavelength and the angle of reflection and depends only on the thickness of the crystal, this being measured perpendicularly to the reflecting planes (Waller⁹ and Stokes and Wilson¹⁰). Similarly, in discussing line-broadening by internal strains, it is convenient to introduce the "apparent tensile strain." This is defined by $\eta = \beta \cot \theta$, which is likewise independent of the wavelength and the angle of reflection. To the approximation to which it has been possible to carry the calculation, the apparent tensile strain depends only on the distribution of tensile strains per-

TABLE III.—Values of Integral Breadth β and of $(\beta \cos \theta)^2$ of Quenched Samples Tempered at 100° C.

19-cm. camera, Co K α radiation, iron filter.

<i>hkl</i> .	Carbon, %.	$\cos \theta$.	Measured Values of—		β , as Calculated for Crystallite Sizes of—		
			β .	$(\beta \cos \theta)^2 \times 10^{-3}$.	100 Å.	150 Å.	200 Å.
200	0.89	0.7795	0.01466	0.13064	0.02290	0.01527	0.01145
	1.20		0.01671	0.14515			
211	0.89	0.6437	0.01997, 0.02045	0.16518, 0.17335	0.02773	0.01849	0.01387
	1.20		0.01947	0.15703			
220	0.89	0.4695	0.03354	0.24794	0.038025	0.02535	0.01901
	1.20		0.02975	0.19509			

unit cells with parameters ($a = 4.5144$ Å., $b = 5.0787$ Å., $c = 6.7297$ Å.) different from that of the adjacent unit cells of ferrite ($a = 2.8604$ Å.) will distort the latter. An expansion of the parameter of ferrite produced in this way is not an indication that it contains carbon in solution. It is easy to visualize the thickening of the cementite plates and of the ferrite blocks in the course of further tempering, which will eventually convert the cementite into small globular grains. This granular cementite will cause less distortion of the adjacent ferrite than the primary plates, so that the parameter of the ferrite must be reduced. A more detailed consideration of the parameter of ferrite in heat-treated samples will be given in the Appendix.

If we regard this simple presentation as correct, then each grain of tempered martensite must be assumed to be a mixture of minute blocks of ferrite and cementite or to consist of ferrite with cementite precipitated in primary shape and size. Owing to the differences in the structure of the two phases (cubic ferrite, orthorhombic cementite)

perpendicular to the reflecting planes, as found by Stokes and Wilson.¹¹

In the above equations λ is the wavelength, θ the Bragg angle, and β the (corrected) "integral breadth" of the hkl reflection. The integral breadth is defined as $\int I d\chi / I_{\max}$, I being the intensity at angle χ and the integration extending over the X-ray line. Some of the values of β and $(\beta \cos \theta)^2$ calculated from photometred lines are given in Table III.

According to A. J. C. Wilson (private communication, March 1945) plotting $\sin^2 \theta$ against $(\beta \cos \theta)^2$ should give a horizontal line if $\epsilon = \text{const.}$ and a sloping line if $\eta = \text{const.}$ The actual line was neither horizontal nor steeply sloping, and it thus appears probable that the broadening of the lines results from both these causes.

It may be assumed that the apparent particle size does not exceed about 150 Å., but more accurate measurements and their evaluation are not yet completed.

Summarizing the results described above, martensite tempered at a low temperature (100° C.) changes over into ferrite (α -iron freed from carbon atoms) mixed with precipitated cementite in primary form (layers, plates). In other words, a martensite tempered under such condition changes over to the first stage of troostite, which should not be called β -martensite, as this would have a cubic structure containing carbon atoms or cementite in solid solution.⁵

ACKNOWLEDGMENTS.

The author wishes to express his best thanks to Professor Sir Lawrence Bragg, O.B.E., F.R.S., for the kind permission to use the X-ray equipment at the Cavendish Laboratory and for his interest in the investigation, to Professor C. W. Dannatt for the provision of laboratory facilities and for his valuable help in preparing the paper, and to Dr. J. F. Allen, and Professor N. F. Mott, F.R.S., for numerous helpful suggestions.

APPENDIX.—Determination of the Lattice Parameter in Heat-Treated Samples.

The measurement of films taken from martensite or tempered martensite samples is very troublesome, as the lines are broadened and diffuse; and there is always the question of what method should be applied to determine the real centre of the broadened line. For this reason Table II. includes not only the $\sin^2 \theta$ values for particular lines but also the variation of the values with 0.1-mm. changes of the reading.

Although the broadened lines are very difficult to measure micrometrically, the curves obtained show peaks, though sometimes indistinct; and the distance between the peaks of two adjacent lines can be taken as corresponding to the distance between these particular lines. The $\sin^2 \theta$ values calculated from 19-cm. and 9-cm. camera films, using micrometer and photometer measurements, are listed in Table II. The most reliable values have been obtained from the 19-cm. camera film and can be checked from the film of electrolytic iron, since the lattice parameter of the latter is well known ($a = 2.8604 \text{ \AA}$).

The films taken from 0.89% and 1.20% carbon steel samples quenched at 780° and 930° C. and tempered for 24 hr. at 100° C. show only a small difference between the parameters of the α -iron unit cells, although the samples were heat-treated in different ways. The extrapolation of $\sin^2 \theta$ (Table II.) up to $\sin^2 \theta = 1$ gives a mean value of $a = 2.8660 \pm 0.001 \text{ \AA}$.

In a further attempt to find a more reliable value for the lattice parameter a sample of the

0.89% carbon steel tempered as described above was covered on two sides with pure iron powder mixed with Canada balsam. Each of the previously very faint and broadened lines showed very sharp additional ferrite lines. In this way two similar substances, i.e., iron in two different conditions, can be compared easily.

The photometer curves of the 220 lines (Fig. 5) indicate a slight difference between the line of the

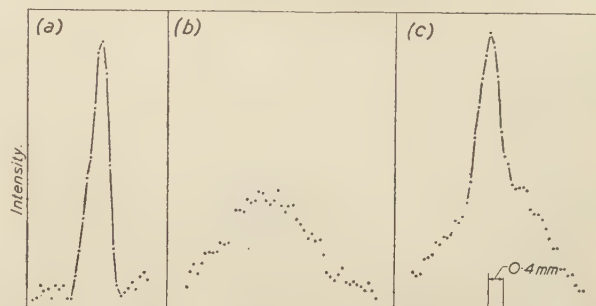


FIG. 5.—Photometer Curves of 220 Lines of (a) Electrolytic Iron Powder, (b) tempered martensite, and (c) electrolytic iron powder plus tempered martensite.

heat-treated sample and that of the iron powder. In other words it shows that there is definitely a slight difference in parameter between the two substances. The position ($\sin^2 \theta$) of the 220 line for iron is well known (calculated from the lattice parameter), so the position of the diffuse line can be determined more easily and more accurately in the way described than by micrometric measurements alone. In this particular case it has been found that when the position of the 220 line is shifted by 0.1 mm., the value of $\sin^2 \theta$ changes by 0.000485. Since by the "combined-substance" method the difference between the positions of the lines has been found to be $0.4 \pm 0.1 \text{ mm}$. (Fig. 5(c)), the lattice parameter can be estimated as $a = 2.8660 \pm 0.001 \text{ \AA}$. This estimation of the parameter by means of the combined substance method has entirely confirmed the previous rough calculation, and the method seems to be very helpful in all cases in which the high angle lines are either missing or too faint and broadened to be used as the basis for the estimation of the lattice parameter by extrapolation, e.g., for $\sin^2 \theta = 1$.

Referring briefly to the structure of heat-treated (quenched and tempered) samples, the observation has been made that the parameter is affected to some extent by variations in the heat-treatment applied as well as by the carbon content and the proportion of it brought into solution. This subject is still under investigation and will be treated separately in a later paper.

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CORRESPONDENCE.

Monsieur A. MICHEL (Chambre Syndicale Française des Aciers Fins et Spéciaux, St. Etienne, Loire) wrote: In contradiction to a theory formulated, especially by Japanese metallurgists, the author has shown that tempering of martensite at 100° C. does not lead to a solid solution of carbon in cubic ferrite—the β martensite of the adherents of the theory mentioned—but to the precipitation of carbon from the tetragonal martensite in the form of cementite, resulting in a mixture of cubic ferrite and lamellar cementite.

The objection against the β martensite hypothesis, already raised by others, seems to be perfectly justified. In fact, the solution of carbon in ferrite—a metastable system—leads to deformation of the lattice of the latter, imparting a tetragonal structure to it, as is to be expected. It is not conceivable how a transformation of this structure can take place at 100° C., leaving the carbon in solution without causing an irregular distortion of the lattice, the geometrical structure of which does not offer symmetrically placed sites for the carbon atom. The conditions governing the solid solution at 20° C. are not modified at 100° C. It is thus not conceivable how the crystallization should change.

However, the author's suggestions regarding the nature of the precipitate, *viz.*, that it should consist of cementite crystals, is not in accordance with previous work. D. P. Antia, S. G. Fletcher, and M. Cohen,* who likewise studied the tempering of martensite, distinguished three well-known stages on tempering at continuously increasing temperatures, namely, the intervals of 95–175° C., 230–290° C., and 290–400° C. The second of these intervals doubtless includes the transformation of the residual austenite, whilst the first is the same as that studied by the author. Whereas he, and other investigators, consider the precipitate formed in this first interval to be cementite, the above-mentioned authors raised a number of

objections against this assumption. They suggested that the precipitate does not immediately consist of cementite crystals but of an intermediary phase which is transformed into cementite only within the third temperature interval, intermediary phases of this kind being known to occur in the decomposition of other solid solutions. The formation of such a transitory phase on tempering of martensite was confirmed by Arbusaw and Kurdjumow,† who, studying single crystals, discovered new lines in their X-ray diagrams after tempering at 130° C.; and these lines disappeared on tempering at 300° C., being replaced by those of cementite.

As early as 1930, P. Chevenard and A. Portevin‡ published a paper on the tempering of austenite and martensite. Dealing especially with a 0.8% carbon steel, water-quenched from 800° C., and taking into account the slight complication of the phenomenon due to the transformation of some 10% of residual austenite, they arrived at the conclusion that the tempering of martensite is a continuous process. Besides, the anomaly of cementite, which appeared on tempering at about 200° C., increased continuously with the tempering temperature, indicating a gradual increase of the cementite formed. The authors stated: "Liberated from the superimposed effect of the decomposition of austenite, the tempering of martensite seems to be a remarkably simple process, in that it consists of a gradual decarburization of the α -iron-plus-carbon solid solution extending over a very wide interval of temperature." In the course of the discussion to which this paper gave rise Broniewski declared that in future the complicated theory of the existence of several states of martensite might be dispensed with.

In their above-mentioned paper Antia, Fletcher, and Cohen report on their examination of the decomposition products of martensite obtained on tempering below 200° C. They found that the

* *Transactions of the American Society for Metals*, 1944, vol. 32, pp. 290–322.

† *Journal of Physics (U.S.S.R.)*, 1941, vol. 5, pp. 101–108.

‡ Congrès International des Mines, de la Métallurgie, et de la Métallurgie appliquée, 6th Session. Liège: 1930.

carbon-bearing constituent possesses no Curie point, which is in accordance with Chevenard and Portevin's results. They further observed that the contraction accompanying the decomposition of martensite is only one quarter of that calculated on the basis of the relative densities of martensite, ferrite, and cementite.

It would be of interest to study the tempering of some martensite freed as far as possible from austenite by quenching at a very low temperature. In this way the complication of the tempering process due to the transformation of residual austenite might be avoided.

AUTHOR'S REPLY.

The AUTHOR wrote in reply: I am very pleased that Monsieur Michel considers the objection to the β -martensite hypothesis justified, in spite of the many contradictory opinions.

The suggestion that there is an intermediate stage in the formation of cementite crystals during tempering must be considered as purely speculative, although the valuable experimental data given by Antia, Fletcher, and Cohen, and by others, should, with further exploration, prove of even greater benefit.

With regard to Arbusaw and Kurdjumov's results, these have not as yet been confirmed by my measurements of the intensity of the background in a large number of films, and I am of the opinion that the cementite lines, even when this phase has been formed, are not detectable, owing to the colloidal size of the particles. This particular subject as well as the real decomposition temperatures of martensite and austenite are now being studied experimentally by Professor

C. W. Dannatt and myself and the results will be reported in due course.

Monsieur Michel's remark that "It would be of interest to study the tempering of some martensite freed as far as possible from austenite" calls for continued effort by many metallurgists whose attempts have so far failed, and other means must be found of solving this particular problem of the structure of tempered steels. However, whether the structure of quenched steels of low carbon content (say, 0.5% of carbon or less) should, in the absence of retained austenite, be regarded as martensite, does not seem to be absolutely certain in view of recent observations on the γ - α transformation.*

I am most indebted to Monsieur Michel for his valuable contribution which proves that a great deal of work has yet to be done before the behaviour of heat-treated iron-carbon alloys can be satisfactorily explained.

* W. J. Wrażej, *Nature*, 1946, vol. 158, Aug. 31, p. 308.

DISSOCIATION REACTIONS WITHIN INCLUSIONS.*

BY CARL A. ZAPFFE, M.S., Sc.D. (BALTIMORE, MD.).

(Figs. 1 to 14 = Plates XVII. to XX.)

SYNOPSIS.

This paper draws attention to two types of fine-scale phenomena operating within non-metallic inclusions which in some cases have an important effect on the metal.

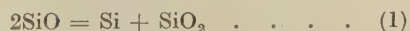
Intrinsic reactions (the first type) are based upon the existence of low-valence non-metallic forms at steelmelting temperatures. Thermodynamically, such systems are isolated, and the compounds spontaneously dissociate during cooling—regardless of the chemical nature of the matrix—into higher-valence compounds plus free elemental metal which may enrich the surrounding steel by dissolving in it. Analogous to the graphitizing of carbon monoxide on cooling, evidence is presented of “siliconizing” in iron-silicon alloys and cast steel, and of “chromiumizing” in stainless steel, this evidence being based on the high-temperature protoxide forms of silicon monoxide (SiO) and chromium monoxide (CrO), respectively.

Extrinsic reactions (the second type) involve included phases which are chemically interdependent with the matrix and are therefore not isolated in a thermodynamic sense. During thermal changes such systems can lead to local redistribution of alloying elements between inclusion and matrix, and the manner in which this takes place may have an important effect on the service or properties of the steel. “Sensitizing” in austenitic stainless steels is one example, and the phenomenon of “flash attack” in certain chromium steels is suggested as another example of commercial importance.

INTRODUCTION.

IN the course of an earlier research by the author and C. E. Sims on the physico-chemical relationships of iron, silicon, and oxygen in liquid steel,^{1,2} an unusual formation of inclusions was reported, an example of which is shown in Fig. 1. The specimen was a 20-g. sample of electrolytic iron containing 0.33% of silicon and brought near to equilibrium with a carefully controlled oxygen-hydrogen atmosphere by soaking at a temperature of 1600° C. \pm 10° for 5½ hr. After dropping the specimen directly into water from this temperature, planetary-type silicate inclusions were revealed, numerous small particles being disposed concentrically outside a larger central inclusion. Two alternative explanations were then proposed for this phenomenon: (1) That the cluster represented growth by agglomeration of the small particles precipitating as reaction products from the cooling liquid; and (2) that instead of agglomeration, the cluster represented dispersion resulting from some chemical reaction taking place within the inclusion during cooling.

As regards this second suggestion, a further proposal was put forward that the reaction involved the decomposition of silicon monoxide to form silica and free silicon:



Although this reaction has an obvious analogy

in the well-established carbon-oxygen equilibrium:



the significance of “siliconizing,” as compared with “graphitizing,” remains to be explored.

Since the phenomenon, if established, would have certain important consequences, it is the purpose of this paper to develop the original suggestion concerning the dissociation of high-temperature low-valence forms of non-metallic elements in steel, and to initiate a new line of thought regarding non-metallic inclusions and minor included phases in general.

OBSERVATIONS WITH SILICON MONOXIDE.

Cleavage Structures of Ferrosilicon

During the development of the metallographic technique referred to as “fractography”,³ the cleavage structures of a series of iron-silicon alloys were studied.⁴ In ζ -phase alloys, an unusual structure consistently appeared having a silicate inclusion as a nucleus surrounded symmetrically by a remarkably circular pattern within the cleavage structure of the ζ phase.⁴ Two examples of this phenomenon appearing in a commercial ferrosilicon containing 50.18% of silicon and 0.12% of carbon are shown in Fig. 4. The slight ovality in Fig. 4(b) is attributable to the elongated, or multiple, nucleus. Clearly, the non-metallic

* Received January 15, 1946.

material has influenced and altered by some means the surrounding sphere of metal, and it has done so at a remarkably constant radial distance. Since the ζ phase has been shown to display consistently and characteristically an elaborately terraced structure,⁴ the absence of that pattern for some radial distance around the inclusion is one indication of the alteration. This phenomenon is immediately explained by the equation (1) (equation (4) of the original paper¹) just quoted. When produced under the very conditions favourable to the formation of silicon monoxide, *i.e.*, high temperature and low oxygen pressure, ferrosilicon would be expected to contain silicon monoxide. In fact, the dioxide (SiO_2) is known to be unstable in contact with alloys of high silicon content at high temperatures, as can be demonstrated by the simple process of heating sand admixed with ferrosilicon.

Fig. 2 shows the result of such a process using 75% of ferrosilicon admixed with quartz sand. An electric arc struck upon a graphite block underneath the mixture caused a marked gasification and a subsequent condensation of the siliceous deposit seen in the figure. Analysis of this condensate corresponds as closely to silicon monoxide as can be determined. An inverted crucible covering the reactants to exclude atmospheric oxygen also became lined with this sublimate.⁵

Some metal collected at the seat of the arc, and the slag layer immediately in contact with that metal was vitreous and yellowish brown, in agreement with numerous recorded observations of SiO .^{2,5} Its analysis again corresponded to SiO . Although Baumann failed to find precise X-ray evidence for SiO in similar material,⁶ his work contains no disproof of its existence. In fact, a commercial silicon monoxide in Germany containing 60–80% of SiO has been available for some time and has served as the basis of some interesting process patents.^{7,8} The failure of the X-ray study is readily attributed both to the instability of SiO at ordinary temperatures and to the presence of atmospheric oxygen, which reoxidizes SiO to SiO_2 and thereby also accounts for the commercial product containing a large proportion of SiO_2 .

Micrographs of the solid substantiate this by showing a pearly admixture of SiO_2 and metallic silicon (Fig. 3). Whether this condition is characteristic only of the polished surface cannot now be determined, but the fundamental process of producing metallic silicon by decomposition of a lower silicon oxide seems unmistakably clear. The phenomenon can be a simple analogy of the decomposition of FeO to Fe_3O_4 and Fe , the FeO offering similar difficulties to observation at ordinary temperatures.

Consequently the present paper proposes that the phenomenon shown in Fig. 4, and probably also that shown in Fig. 1, represents the *precipitation*

of a lower oxide with subsequent decomposition forming a higher oxide and simultaneously liberating free metal.

The factor of greatest metallurgical significance is, of course, the liberated metal, for its absorption into the surrounding matrix will change the composition of the alloy in that region until diffusion completes itself. We are therefore witnessing *siliconizing* from the decomposition of silicon monoxide, which is analogous to the more commonly observed "graphitizing" from the decomposition of carbon monoxide.

The hypothesis can be checked fractographically because the variation of the fracture pattern with the silicon content of iron-silicon alloys is fairly well known.⁴

In Fig. 5 two superimposed fractographs have been taken of a large silicate inclusion; what appears to be a silicon-rich phase can be seen between the inclusion and the ζ phase. Two pictures were required to obtain focus both on the pattern of the surrounding ζ phase and on the lower-level intermediate residual phase. This intermediate phase has a cleavage pattern obviously unlike the ζ phase and entirely consistent with the high-silicon θ phase.⁴ It should be noted how obviously more brittle is the interior phase—in keeping with its higher silicon content. The figure therefore probably depicts the emigration of silicon from the inclusion in quantities sufficient to change locally the ζ phase to the θ phase. Since a silicon content of 96% is necessary to produce the θ phase, it is consistent that this change is only noted around large inclusions. With increasing volume of the inclusion the potential surface concentration of emigrating silicon increases, of course, and it does so roughly as the power of $\frac{3}{2}$. For lesser emigrations the surrounding matrix remains in the ζ phase, but its increased silicon content brings about secondary cleavage changes similar to those in the α phase⁴ and a circular pattern results.

In Fig. 6 another aspect of this phenomenon appears which is included for its possible qualitative significance. Here a channel-type break in the ζ -phase pattern proceeds from a deep dendrite arm up to the circle. The suggestion is that a protoxide inclusion formed in the liquid and levitated until trapped, decomposed during levitation to cause a compositional change in its path sufficient to influence the fracture pattern of the ζ phase, but insufficient to produce the extremely silicon-rich θ phase.

By similar reasoning one finds an explanation for another unusual observation, which is shown in Fig. 7. A sample of this same ferrosilicon was heat-tinted at 1000° C. (1832° F.) in air for several minutes. White circular areas were observed amidst the brownish iron silicate covering the rest of the specimen (Fig. 7(a)). This seems to be



FIG. 1.—Cluster-Type Silicate Inclusion in Deoxidized Electrolytic Iron. $\times 3000$.

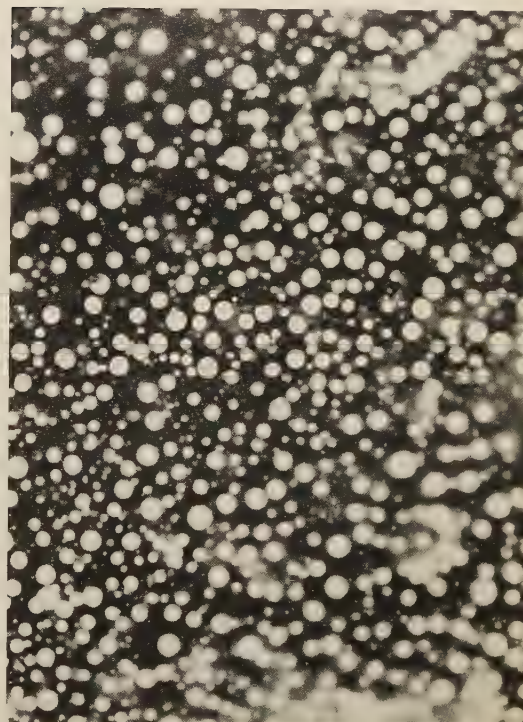


FIG. 3.—Vitreous Silicon Monoxide Residue, showing admixture of Si and SiO_2 . $\times 2000$.



FIG. 4.—Fractographs of Commercial 50% Ferrosilicon, showing the unusual structure surrounding silicate inclusions in the ζ phase. $\times 2000$.



FIG. 6.—Fractograph Showing Channel-Type Break in the ζ Phase. $\times 500$.

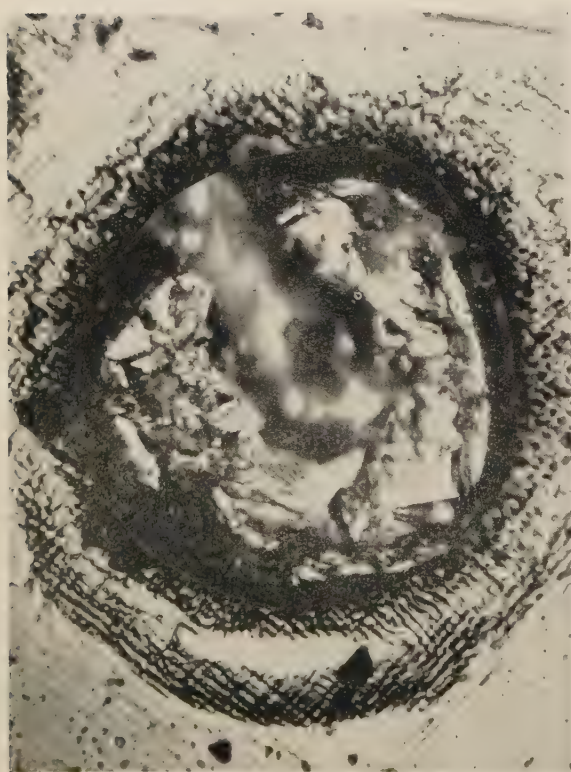
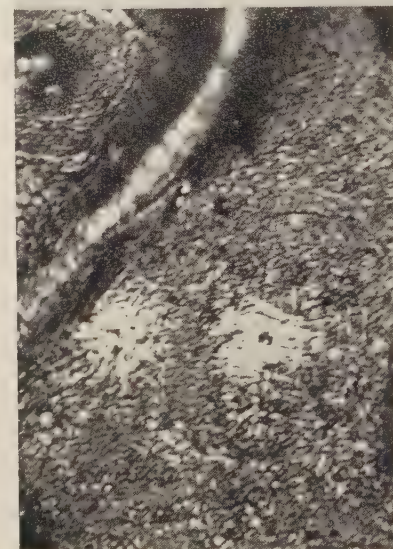
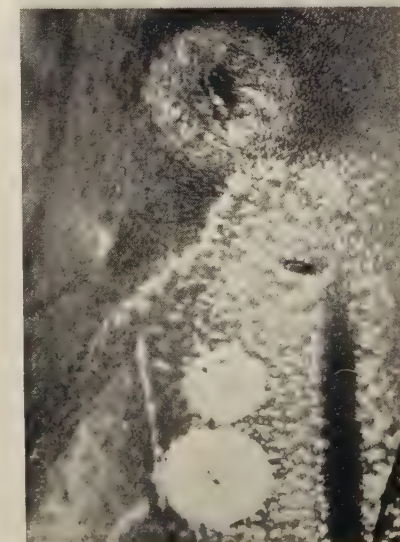


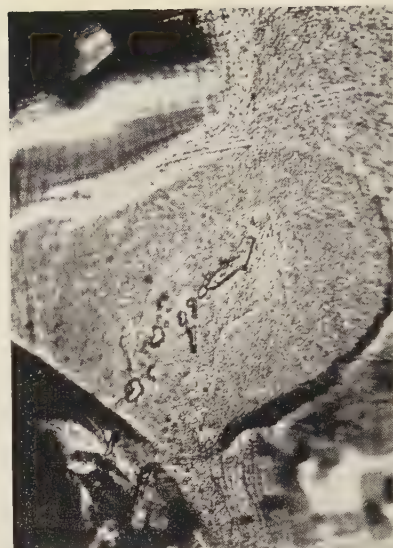
FIG. 5.—Two Superimposed Fractographs of a Large Silicate Inclusion in Ferrosilicon. $\times 400$.



(b)



(a)



(c)

FIG. 7.—Fractured 50% Ferrosilicon Revealing Silicon Enrichment (a) after heat-tinting a few minutes at 1000°C ., (b) after annealing 1 hr. at 1000°C ., and (c) as (b), showing almost complete homogenization around silicates. All $\times 500$.



FIG. 8.—Ferrite Sheaths Surrounding Silicate Inclusions in Pearlitic Cast Steel (Sims), $\times 1000$.

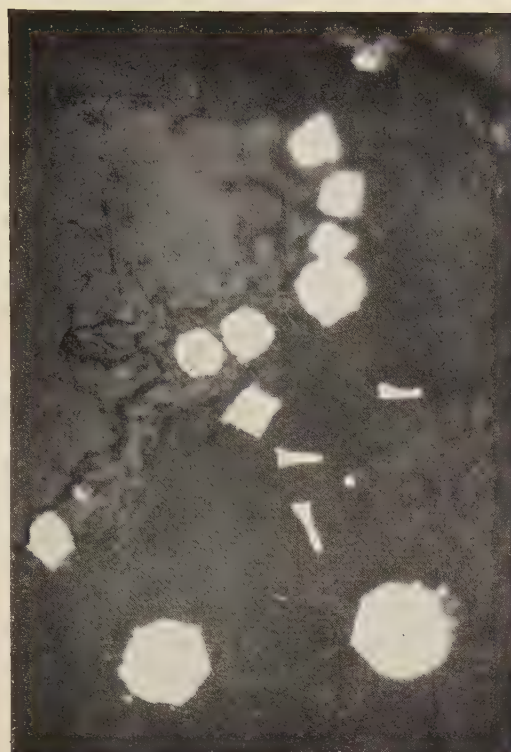


FIG. 9.—Semi-Reduced Chromium Oxide, showing two oxide phases with particles of metallic chromium in the darker phase only, $\times 1000$.

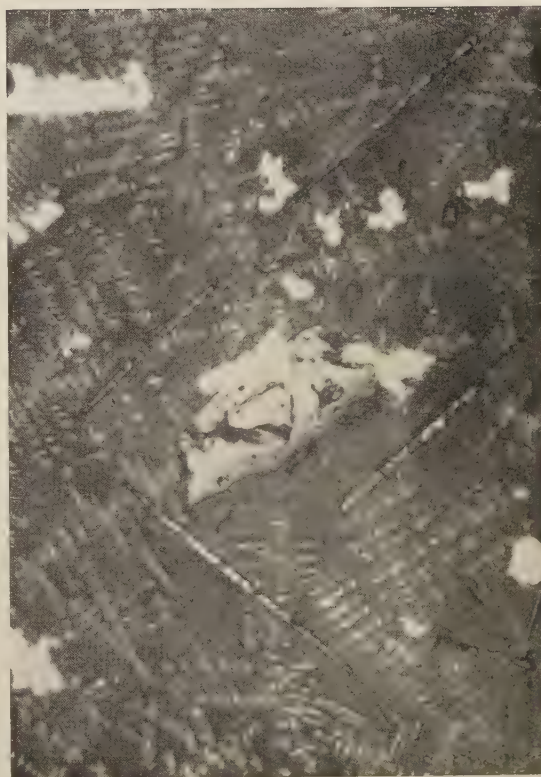


FIG. 10.—Dark Secondary-Oxide Phase Illuminated to Show Dendritic Network, $\times 1000$.



FIG. 11.—Higher Magnification of the Dendrites Shown in Fig. 10, $\times 2000$.

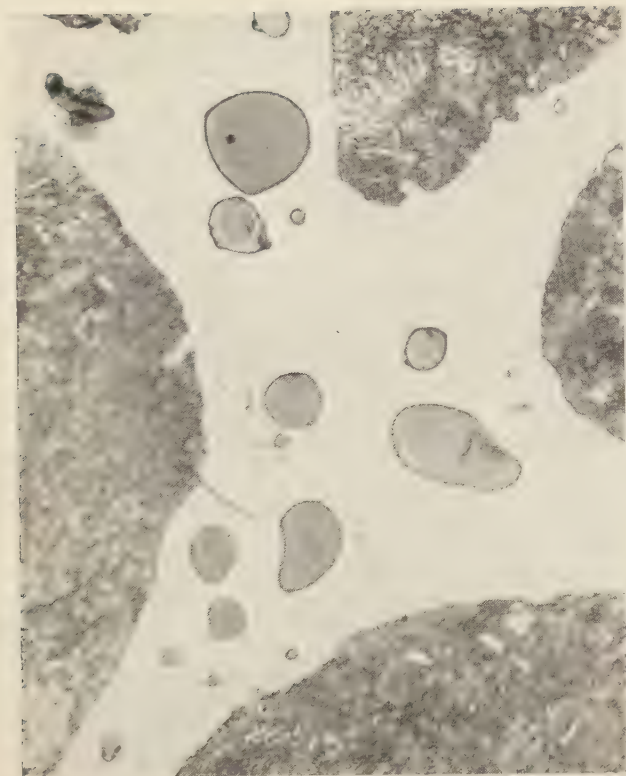


FIG. 13.—Cast Pearlitic Steel, showing grain-boundary sulphides surrounded by ferrite (Sims). $\times 1000$.



FIG. 12.—17% Chromium Steel, showing metal inclusions within chromite inclusions. $\times 3200$.



FIG. 14.—“Flash Attack” along Sulphide Inclusions in Stainless Steel; (a) $\times 500$, and (b) $\times 2000$.

direct evidence of silicon enrichment. When heated for 1 hr., however, at 1000° C., the specimens showed either diffusive white areas (Fig. 7(b)), or none at all (Fig. 7(c)).

C. E. Sims of the Battelle Memorial Institute has called to the author's attention a long-unexplained phenomenon in silicon-killed cast steel, a sample of which is shown in Fig. 8. This steel (containing 0.52% of carbon, 1.38% of manganese, 0.17% of silicon, 0.305% of sulphur, and 0.008% of phosphorus) showed ferrite sheaths surrounding silicate inclusions imbedded in pearlite. Sims points out that the silicon enrichment around those inclusions from decomposing SiO would raise the A_{r_3} point above that of the surrounding metal and that, in slow cooling, that region would transform earlier, the carbon migrating into the surrounding austenite. To this, the author would add that the similar spots recently reported by Binnie⁹ in a shell-steel ingot now become explained. In fact, the ferrite sheaths discussed by Schofield¹⁰ might also be related to this phenomenon.

OBSERVATIONS WITH CHROMIUM MONOXIDE.

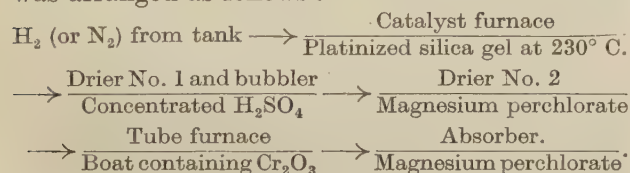
Evidence of "Stepwise" Reduction.

A high-temperature chromium protoxide (CrO) has been described by numerous investigators over a number of years,⁵ although metallurgists have not yet given it their attention. Decomposing during cooling, chromium monoxide would produce metallic chromium and the sesquioxide according to the reaction:



which is analogous to the previous equation and represents *chromiumizing* from spontaneous thermal dissociation of protoxide chromites.

This metallizing reaction and the rôle of chromium monoxide seem to be descriptively illustrated in the following experiment. A gaseous reduction train typical of ore-reduction studies¹¹ was arranged as follows:



An alundum boat filled with chemically pure Cr_2O_3 (8.7522 g.) was baked at 500° C. for 20 min. along with two silica reflectors later to be placed about 2 in. off each end of the boat in the furnace to prevent terminal heating. After the boat and the reflectors were placed in a McDanell furnace tube with a platinum/13% rhodium thermocouple supported through one reflector to keep its tip directly above the centre of the boat, the train was flushed with nitrogen. When the heating was

begun the hydrogen replaced the nitrogen, flowing at a rate of 8–10 litres/hr. Periodic weighings of the absorption tube served as a measure of the reduction.

Below about 1400° C., reduction was insignificant. Over a period of 125 min. the temperature was raised from 1400° to 1610° C., when the test was discontinued. The oxide was then furnace-cooled in hydrogen to room temperature. During the test 0.2897 g. of H_2O was produced, which represents a removal of 0.2535 g. of oxygen—the equivalent of 0.845 g. of Cr_2O_3 reduced to Cr, or of 2.54 g. of Cr_2O_3 reduced to CrO.

Inspection of the residue showed no visible metal, but for a considerable depth from the surface (consistent with the calculation just made for reduction to CrO) the oxide had changed from the characteristic chromic green to a deep bluish black. Reheating a portion of this material for 10 min. at 1150° C. in air reproduced the chromic green colour, presumably through reoxidation of CrO to Cr_2O_3 . When the sample was examined under the microscope, particles of metal were visible, but only within the dark secondary oxide, as shown in Fig. 9. Furthermore, a stronger illumination of this secondary, bluish-black oxide showed the metal particles lying amidst a pattern of fine dendrites having considerable reflectivity (Fig. 10). At higher magnification (Fig. 11) these dendrites were shown to contain minute metallic particles (Cr) imbedded in narrow dendritic regions of the light grey phase characteristic of chromite inclusions in steel and identifiable as the Cr_2O_3 phase. In addition, a few larger particles of metallic chromium were present, perhaps because of coalescence, but more likely because the experiment was not performed under equilibrium conditions. That is, the oxygen pressure (P_{O_2}) of the incoming purified hydrogen could momentarily and locally be less than the P_{O_2} even of CrO, causing locally some complete reduction.

It is suggested that the hydrogen first reduced the Cr_2O_3 to CrO, just as it reduces Fe_3O_4 to FeO at temperatures above 565° C.,¹¹ and that, on cooling, this CrO decomposed to form dendrites comprising fine particles of metallic chromium admixed with Cr_2O_3 , which in turn were imbedded in undecomposed CrO.

The dissociation of FeO provides a known analogy:



Oberhoffer and d'Huart¹² found metallic iron separating in dendritic form from within mill-scale furnace-cooled from 1380° C.

Significance of the Dissociation of Chromium Monoxide.

More than a decade ago Portevin¹³ called attention to "inclusions within inclusions" found in

a 30% chromium steel of low carbon content. The inclusions were complex chromium silicates, and within them were metallic particles precipitated variously as dendrites, cubic crystals, or as a eutectic cloud. Matuschka¹⁴ made a similar observation with the inclusions in ferrochromium. Neither recognized, however, that the particles could represent the product of a stoichiometric dissociation reaction, the only explanation ever given being based on a supposed slight solubility of the metal in the oxide.

In Fig. 12, the two "chromite" inclusions in a 17% chromium steel contain metallic particles. Once looked for, such cases are rather numerous, and though in some cases it is true that one observes a planar section through a re-entrant arm of the matrix, that classic refutation should now be recognized as being insufficient. Even in Fig. 12(b) (which is the less convincing of the two) the metal arm more likely extends *from* the inclusion rather than into it, since chromites are predominantly primary inclusions which form before the metallic dendrites and therefore are not likely to exhibit conformity to such dendrites.

Thus in certain "balanced" chromium-nickel steels a class of phenomena should exist comparable to that of the ferrite sheaths described by Sims for cast carbon steel. That is, the production of chromium from dissociating protoxide in balanced austenitic grades should form local ferritic chromium-rich patches which might have an important effect on the steel.

Similarly, passivity should be favoured at those locations in steels containing chromium in the critical passivity-activity range of 11-13%.

Undoubtedly certain anomalies in the service or behaviour of stainless steel relate to this "chromiumizing" function and remain to be explored. Their further discussion, however, is beyond the scope of this introductory paper.

In another field, the abnormal firing expansion, high porosity, and crumbling of chromite refractories in reducing atmospheres, as reported by Lynam, Howie, and Chesters,¹⁵ may be related to the reduction of Cr_2O_3 to a secondary slag form containing CrO .

FURTHER OBSERVATIONS.

Dissociation of Other Oxides.

Klemm and Grimm¹⁶ have reported that vanadium similarly forms a monoxide (VO) which dissociates into metallic vanadium and a higher oxide. The author's observations therefore seem reliably multiplied to include all metal oxides reported to have protoxide forms at high temperatures.⁵

As a consequence, a wealth of possibilities remains for research on specific systems. It is even

possible that the metallic particles persistent in slags have some relation to protoxide decomposition, rather than to the purely physical action of ebullition.^{17, 18}

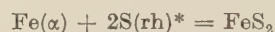
The Dissociation of Sulphides.

Besides oxides, the analogous sulphides should be considered. It is interesting to note that Wilkins¹⁹ reports secondary metallic inclusions within iron-manganese sulphides. Iron forms monosulphide (FeS), and disulphide (FeS_2), and possibly others, such as Fe_2S_3 . As with monoxides, the monosulphide is favoured by high temperatures.

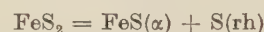
No attention ever seems to have been paid to the possible dissociation reaction :



However, Kelley²⁰ discusses the following reactions :



$$\Delta F^\circ = -38,350 + 1.36T \log T + 2.75 \times 10^{-3}T^2 + 3.48T.$$



$$\Delta F^\circ = 16,080 + 11.72T \log T - 15.94 \times 10^{-3}T^2 - 35.64T$$

from which the following can be calculated :



$$\Delta F^\circ = +6,190 - 24.80T \log T + 29.13 \times 10^{-3}T^2 + 67.80T.$$

This free energy expression shows a positive value of +41,680 cal./mol. at 1000° C., which becomes less positive with decreasing temperature. Consequently the dissociation of FeS into FeS_2 and free Fe is possible during cooling.

On the other hand, ΔF° is still +10,360 cal./mol. at 0° C. This is equivalent to less than 10% dissociation. Otherwise, one might seriously propose that the sulphide inclusions commonly observed surrounded by grain-boundary ferrite is a *cause* of that ferrite rather than an accompaniment (see Fig. 13).

REACTION OF INCLUSIONS WITH THE MATRIX.

The chemical behaviour of included phases may be classified under two types : (1) Intrinsic reactions occurring from thermal or barometric changes and having no dependence upon the chemical nature of the surrounding matrix, and (2) extrinsic reactions based on chemical interdependencies with the matrix. The first type is represented by the dissociation reactions already discussed.

The second type of reaction remains to be explored. The non-metallic inclusion and the matrix each contain at least two metallic elements

* Denotes rhombic sulphur.

which are distributed chemically between the two phases and have characteristic temperature functions with respect to the non-metallic elements to which they are bound. The wide interval between the temperature of solidification of the ingot (at which inclusions form) and that of the subsequent annealing and hot-working allows a possible redistribution of the metallic elements across the phase boundaries.

For example, a steel containing 12% of chromium is on the activity-passivity borderline. Sulphur added to such a steel for purposes of free-machining often causes a corrosion phenomenon known as "flash attack" to occur when the steel is immersed in HNO_3 . Under the microscope, the attack is seen to be localized alongside sulphide inclusions. Fig. 14 shows this attack in a stainless steel (type 416 *) containing 13.88% of chromium; the steel had been annealed for 1 hr. at 1550° F., cooled at the rate of 50°/hr. to 1300° F., air-cooled to room temperature, polished, and etched for 1 min. in HNO_3 at 25° F.

An explanation for this phenomenon according to the present hypotheses is that the sulphides form in the liquid steel with a given chromium-manganese-iron ratio, but that with decreasing temperature the affinity of chromium for sulphur increases more rapidly than does that of manganese and iron. The matrix immediately surrounding the inclusion then loses chromium to the inclusion and local chromium impoverishment results. This impoverishment is similar to the "sensitivity phenomenon" in austenitic stainless steel caused by the difference in the temperature functions of the carbides of iron and chromium.

CONCLUSION.

Attention has been drawn to a new class of phenomena having both theoretical and practical significance which involves chemical activity in occluded minority phases, specifically non-metallic inclusions in iron and steel.

Two types of chemical activity have been discussed: (1) *Intrinsic* reactions which are thermodynamically isolated and independent of the matrix and are based upon the existence of low-valence forms developing at high temperature, and (2) *extrinsic* reactions which follow from changes in the constitutional interdependency of the inclusion and the matrix with change in temperature.

Reactions of the first type (analogous to the graphitizing of carbon monoxide on cooling) produce free Si from SiO and free Cr from CrO according to the reactions:



The consequent "siliconizing" explains the

ferrite sheath often found surrounding silicate inclusions in cast pearlitic steel, and it explains certain phenomena observed in studying the cleavage facets of ferrosilicon alloys by the new micrographic technique known as fractography. The rôle of CrO similarly seems an important one in the reduction of Cr_2O_3 , and perhaps in stainless steel.

The analogous dissociation of low-valence sulphides warrants exploration.

Extrinsic reactions have received previous attention, notably in the case of "sensitization" in austenitic stainless steel. A reaction of this general type involving sulphides seems acceptable for explaining the phenomenon of "flash attack" in free-machining 12% chromium steel.

ACKNOWLEDGMENT.

The author wishes to thank Mr. Mason Clogg, jun., of the Rustless Iron and Steel Division, Armco, Baltimore, Maryland, for his assistance in the photographic details of this work.

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CORRESPONDENCE.

Mr. L. G. HUGGETT (Philips Research Laboratories, London) wrote: As a chemist engaged in research in arc-welding, it has seemed to me for some time since the original work of Zapffe and Sims * at the Battelle Memorial Institute on the silicon-oxygen equilibrium in liquid steel, that the possibility of the formation of silicon monoxide in liquid weld metal is most important in its implications. The evidence in favour of the monoxide theory seems to be considerable, and the extension of this theory by Dr. Zapffe to include the lower oxides of other metals, chromium and vanadium and possibly also titanium, the oxide of which is widely used in coated welding electrodes, is most interesting. When more experimental information is available on the conditions under which these compounds are formed in liquid steel, that is, particularly the free energies of formation at varying temperatures, it will be possible to see more clearly the rôle of these lower oxides in the steelmaking processes and particularly the more complex arc-welding process, and their influence on the properties of weld metal.

It appears to me that the information already available on silicon monoxide indicates that it may have an important influence on the properties of weld metal. The conditions in arc-welding are ideal for the formation of silicon monoxide and the other lower oxides if they behave similarly. According to the work of Zapffe and Sims * a high temperature favours the formation of silicon monoxide. Although in most mild-steel electrodes the core wire is usually a rimming steel, and ferro-silicon is not often used, silica is almost invariably present in fairly large amounts in the coating. Further, it is well known that in spite of this some electrodes with rimming-steel core wires can produce welds containing high percentages of silicon. It can be concluded that, in spite of the short time available for reaction at the high temperature of the arc, silicon in some form passes into solution in the steel to an appreciable extent. It seems now that this form is probably largely the oxide SiO. It is conceivable that a similar process occurs with the lower oxides of other metals.

As the liquid steel cools, the tendency will be for the monoxide to decompose, forming silicon and silica. The rate at which this decomposition takes place must be extremely rapid. This is demonstrated by the presence of the small inclusions of silica in Dr. Zapffe's water-quenched samples.* However, it is possible, and indeed quite likely, under conditions of very rapid cooling, as in welding, that some degree of supersaturation occurs. The metastable condition

which results may have a considerable influence on some of the important physical properties of weld metal, particularly crack sensitivity and ageing, apart from the effect on the general mechanical properties of tensile strength, ductility, and impact strength.

It is known that in several types of weld metal total silicon analysis does not represent all metallic silicon. Vacuum-fusion analysis of welds and chemical and X-ray analysis of iodine extraction residues have shown conclusively that silicon is often present largely as silica. This is shown in Sloman's † recent work. In some welds containing about 0.06% of silicon this was almost completely in the oxidized form.

This silica is in the form of very fine inclusions, often of silicates, which are undoubtedly formed as a result of chemical reaction during cooling and cannot be caused by mechanical entrapment of slag particles. The fact that the reaction



proceeds further to the right as the temperature falls, would be sufficient to explain the presence of small inclusions of silica or silicate, and from the viewpoint of equilibrium conditions at comparatively low temperatures, when SiO is unstable, it would be sufficient to consider only this reaction between iron oxide and silicon to form silica. However, the reaction mechanism is most important in a study of the chemistry of steelmaking and perhaps even more so in a study of welding. Clearly, the reaction written above cannot explain the presence of any silicon-rich areas around inclusions in the cases cited in the present paper. In fact one might more reasonably expect to find a deficiency of silicon.

There is, as yet, too little information on the composition of weld metal and the form in which the components are present, to point to any definite indication that silicon monoxide or any other lower oxide has any such influence as has been suggested. This is only one of the problems that must await more detailed experimental data on weld-metal composition.

Dr. D. BINNIE (The Lancashire Steel Corporation, Ltd.) wrote: The author points out that the white spots of precipitated ferrite surrounding non-metallic inclusions are explained by presuming an absorption of silicon from decomposing SiO. The silicon enrichment will then raise the Ar₃ point and thus, on cooling, carbon would migrate into the surrounding austenite, leaving a ferritic sheath or spot round the non-metallic inclusion.

In the discussion on the paper,‡ "A Study of a

* C. A. Zapffe and C. E. Sims, *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1943, vol. 154, p. 192.

† H. A. Sloman, T. E. Rooney, and T. H. Schofield, *Journal of The Iron and Steel Institute*, 1945, No. II., p. 129 P.

‡ D. Binnie, *Journal of The Iron and Steel Institute*, 1944, No. I., p. 353 P.

Shell Steel Ingot," two speakers were also inclined to the view that the white spots of precipitated ferrite arose from the raising of the critical point, but this raising of the critical point was attributed to phosphorus.

If the raising of the critical point was due to phosphorus, or to silicon, then the writer would think that this microscopic and local increase would persist throughout a normalizing treatment, *i.e.*, at normalizing temperatures there could hardly be any appreciable diffusion of the phosphorus or silicon, and the white spots or sheaths should reappear in some form or other on cooling from a normalizing temperature. Normalizing was done on a specimen cut from the ingot and the structure (*see* Fig. 59 of the writer's paper (*loc. cit.*, plate XXXII.)) showed that the white spots had disappeared. The actual specimen was re-examined at higher power, $\times 500$, and again there was no evidence of the cluster of white spots seen on the as-cast steel.

The writer would like to draw attention to the distribution of the white spots in the as-cast structure of the ingot. This has been described in some detail on pp. 363 P–364 P of the writer's paper (*loc. cit.*). Here it was stated that the spots were virtually absent from the feeder head, but at the top of the ingot just below the feeder head, and also at the middle height of the ingot, the spots were present immediately below the skin. In the

ingot cuts from the bottom end of the ingot the white spots did not really appear until 0.3–0.4 in. below the skin and then only as a narrow column of spots. At about $\frac{1}{2}$ in. in from the skin the white spots in these bottom ingot positions suddenly appeared in cloud form.

The occurrence of the spots does not follow any of the usual known laws of crystallization, but the writer has in mind that they are positioned by some critical rate of cooling. The spots are not present, at least to any extent, in the surface equiaxed chill zone, which zone is only present to any extent in the bottom half of the ingot.

Similar white spots have been reported by Law and Harbord* when they said that individual sulphide grains embedded in pearlite were frequently surrounded by a circular ring of free ferrite, especially in the more rapidly cooled parts near the outside of the ingot (*see* Fig. 12 of the Law and Harbord paper). Here the white spot was associated with a sulphide inclusion and if the white spot had been caused by a diffusion into the neighbouring ferrite by means of a dissociation reaction within the inclusion, then the diffusion in this instance would have resulted in a lowering of the critical point by manganese from the sulphide inclusion, which is rather against the view that the spots were a result of raising the critical point, as suggested in the author's paper as an explanation for the presence of white spots.

AUTHOR'S REPLY.

The AUTHOR wrote in reply: Mr. Huggett's and Dr. Binnie's contributions to this paper are much appreciated. Mr. Huggett mentions titanium protoxide rather hesitatingly. However, titanium forms a monoxide probably more readily than does silicon; and TiO has been rather widely studied. Besides Kreimer's work,¹ mentioned in reference No. 5 of the paper, there is Wentrup and Hieber's identification of TiO in the deoxidation of liquid steel,² Belyakova's X-ray identification of TiO resulting from the hydrogen reduction of TiO₂,³ Meerson's production of TiO by carbon reduction of TiO₂,⁴ and Naylor's⁵ and Shomate's⁶ thermodynamic studies of TiO, Ti₂O₃, and Ti₃O₅ over a wide temperature range.

In weld metal, the rôle of protoxides remains to be explored. However, the matter of crack sensitivity mentioned by Mr. Huggett is believed by this writer to be a function of hydrogen content and internal stress,⁷ requiring no participation by protoxide, although the decomposition reactions could conceivably become a factor in cracking through augmentation of stress.

No answer is forthcoming to Dr. Binnie's comment on normalizing. A change in composition

at the locus of the white spot seems required for its disappearance, regardless of the time given to effect that change; and an interchange across the phase boundary holds a ready answer. As for sulphide activity, it is possible that an element other than manganese is ejected on cooling, either iron itself, or perhaps phosphorus.

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* T. E. F. Law and V. Harbord, *Journal of The Iron and Steel Institute*, 1943, No. II., p. 489 P. M

NEW ANNEALING PLANT FOR STEEL STRIP IN COILS AT THE WHITEHEAD IRON AND STEEL CO., LTD., NEWPORT, MON.*

BY B. JONES, D.Sc. (WHITEHEAD IRON AND STEEL CO., LTD., NEWPORT, MON.) AND I. JENKINS, M.Sc. (RESEARCH LABORATORIES, GENERAL ELECTRIC CO., LTD., WEMBLEY).

(Figs. 3 to 11 = Plates XXI. to XXVI.)

SYNOPSIS.

An electric unit for the annealing of steel strip in coils in a controlled atmosphere is described. The plant was designed for an output of 1000 tons/week, and is worked in conjunction with a similar and older installation with an output of approximately 500 tons/week. The compact layout of the plant, which includes sixteen annealing furnaces, recuperator and cooling pits, and controlled atmosphere units, is referred to. Details of the annealing cycle are given, and the causes of staining of the steel charge by unsuitable annealing gas and rolling oils are discussed. There is a close control of temperature in both the furnace and the charge. Tests have been made on the properties of low-carbon steel strip annealed in various parts of the annealing container, and an Appendix is given on the effect of annealing temperature on the properties of heavily cold-reduced mild-steel strip. It is shown that there is a range of annealing temperatures above 600° C. in which the work-hardening effects are effectively removed, good properties are obtained, and a suitable grain-size can be imparted to the steel.

A NEW electric annealing plant was installed at the works of the Whitehead Iron and Steel Co., Ltd., Newport, Mon., in 1944, for the bright-annealing of cold-rolled mild-steel strip in coils. The plant was designed for an output of 1000 tons/week, and it incorporates many new features based on experience with a similar and older installation with an output of approximately 500 tons/week. Both plants consist of the vertical cylindrical or batch-type furnaces, and the new installation alone represents the largest of its kind in this country. It may be of interest to refer to the developments in the production of hot- and cold-rolled strip at the Newport works of the Company, leading up to the necessity for the provision of a large annealing plant for heat-treatment.

The Hot-Strip Mills.

A continuous narrow-strip mill (No. 2 mill) was installed at Newport, Mon., in 1922. This mill was supplied by the Morgan Construction Co., of Worcester, Mass., U.S.A., and was one of the first of its type to be erected in this country. The design was influenced by the experience gained on the original semi-continuous mill put down by the Company at Tredegar, Monmouthshire, in 1907, and by the continuous hoop and skelp mills developed by the Morgan Construction Co. in the U.S.A., the main features of which were in-

corporated, with certain modifications, in the design of the plant. The rolled strip leaves the finishing stand at a speed of approximately 1500 ft./min. and is reeled into coils. A further bar and strip semi-continuous merchant-mill (No. 3 mill) was installed in 1931, and includes the rolling of round bars of up to 2-in. dia., and of strip up to a width of 8 in.

The First Cold-Strip Mills, and Old Annealing Plants.

A cold-rolling plant was installed in 1924 as an auxiliary to the No. 2 continuous hot-strip mill. The Robertson mills consisted of four lines, each containing four stands in tandem, for the production of cold-rolled coiled strip up to a width of 4 in. The cold-rolling plant was provided with separate bays for the processes of pickling, slitting, and annealing. The original annealing plant was comparatively crude, consisting of a 6-cell coal-fired annealing furnace dealing with coils up to 24-in. in dia., which were contained in pots with luted covers. Later, a similar furnace, treating coils of up to 36-in. in dia., was installed, together with a box annealing furnace for the heat-treatment of straight lengths. The temperatures were indicated by recording pyrometers. Attempts were made to reduce oxidation of the charge to a minimum by packing cast-iron borings around the coils of strip but, in view of the labour involved and the unpleasant

* Received February 4, 1946.

working conditions, the bright-annealing was later carried out by introducing coal gas during the annealing period. In these early days it was a difficult matter to retain a bright surface on the strip, and the process was far from satisfactory, owing to sooting and blueing of the charge.

The advantages of electric furnaces for the annealing of cold-rolled coils were realized at an early date and, in 1934, six vertical cylindrical furnaces were installed by the General Electric Co., Ltd., to service the No. 2 cold-rolling mills, three of these furnaces having effective loading diameters of 36 in., two of 28 in., and one of 20 in., together with recuperators and cooling pits. Details of the furnaces and the separate annealing containers are given later in the paper. In these early days the use of a controlled atmosphere for bright annealing was considered to be unnecessary. Many experiments were carried out to reduce the oxidation of the steel charge to a minimum. For some time, the evaporation of the oil from the steel strip was used to generate within the pot an atmosphere that would maintain the bright surface finish as far as possible. For this purpose, a gas vent was provided at the top of the pot, the vent being fitted externally with a non-return valve which allowed the discharge of the oil vapours produced by evaporation, and the escape of air by thermal expansion during slow heating. The oxidation by the air present in the container was not excessive, owing to the relatively small amount of free space compared with the surface area of the steel charge, and any oxidation that did take place was cleaned up by the reducing gases in the oil vapours. During the cooling period, the non-return valve was screwed down, thus giving a gas-tight pot, in which the charge was cooled under a partial vacuum created by the contraction in volume of the atmosphere. The results obtained were very promising, but yet not totally satisfactory.

Development of the Cold-Strip Mills and Annealing Plants.

In 1937, the cold-rolling, pickling, and annealing plants were increased. A 4-high Lamberton United reversing mill, the first in this country, was installed in No. 4 bay for the cold-reduction of coiled strip up to 14 in. wide. Soluble oil was used as a lubricant in this mill. At the same time a further four electric furnaces, two with effective loading diameters of 44 in., and two with corresponding diameters of 36 in., were installed in No. 4 bay. The annealing containers were modified to permit the circulation of a controlled atmosphere of partially burnt town's gas, produced in a separate unit delivering 300 cu. ft. of gas/hr. This output was found to be sufficient to supply the gas for the four furnaces, the pre-purging of

the loaded containers before charging into the furnaces, and the cooling pots. One of the advantages in the use of the controlled atmosphere was in driving out the oil vapours as rapidly as possible from the annealing pot. In the absence of a gaseous atmosphere, the vapours driven off from the interior of the coil dissociated on the hotter outside surfaces, from which the oil had already evaporated. During the cooling period, the non-return valve was still used to seal the pots, which remained connected to the supply of annealing gas, and were thus cooled under a pressure, and not in a flow, of gas. The bright-annealing thus obtained was found to be markedly superior to that obtained with the former methods.

Additions to the No. 4 bay cold-rolling plant were made in 1939 by the installation of a 4-stand Davy United tandem mill for rolling strip up to a width of 14 in., in coils, and two single-stand mills of the same size for temper rolling. The tandem mill is adapted for use as a 3-stand when required, by the inclusion of an additional reel after the third stand. At the same time, the six electric furnaces from No. 2 bay, and the four from No. 4, were transferred to No. 5 bay. In 1940, the annealing plant was completed, and now includes 13 furnaces, giving a normal output of up to 550 tons/week, although, during the last war, the output exceeded 600 tons/week on occasions. The furnaces are of various sizes for heating annealing pots with effective loading diameters of 44 in. (four), 36 in. (five), 28 in. (two), 24 in. (one), and 20 in. (one). Three gas burners, each delivering 500 cu. ft. of burnt town's gas per hour, have replaced the original smaller units, two burners being sufficient to supply the needs of the plant, with one burner in reserve.

Pickling of the hot-rolled coils is carried out in Taylor plants after a loose re-coiling to open out the coils. A feature of the process is that it has been worked, since 1939, in conjunction with a Kestner acid-recovery plant.

During the period 1944-1945, a further extension of the cold-rolling plant was made in No. 6 bay by the addition of a Davy United 3-stand tandem mill, rolling strip of up to 14 in. in width at a speed of 1200 ft./min., and a Davy United reversing mill for the cold-reduction of strip of up to 21 in. in width. The modern mills are designed for the production of cold-rolled strip in coils by continuous high-speed rolling, and are equipped with the latest devices for the control of the strip gauge by means of flying micrometers, and for the automatic regulation of tension in the strip by Metadyne control, &c. Various temper mills for the rolling of the annealed coils have been incorporated, together with slitting machines, equipment for cutting the coiled strip into lengths, and roller-levelling machines.

THE NEW ANNEALING PLANT.

Layout.

In the general layout of the plant, the primary considerations have been maximum compactness and flexibility, with ready accessibility to all the key points of the installation. A diagrammatic plan and section of the general layout is given

120 kW., and take annealing containers having internal dimensions of 36-in. dia. \times 74-in. deep. The remaining 10 furnaces are of larger size, each rated at 130 kW., and take containers of 44-in. internal dia. \times 74-in. deep. A raised platform of steel checker-plate is built around the furnaces, providing ready access to any part of the installation, and this platform is extended to include the

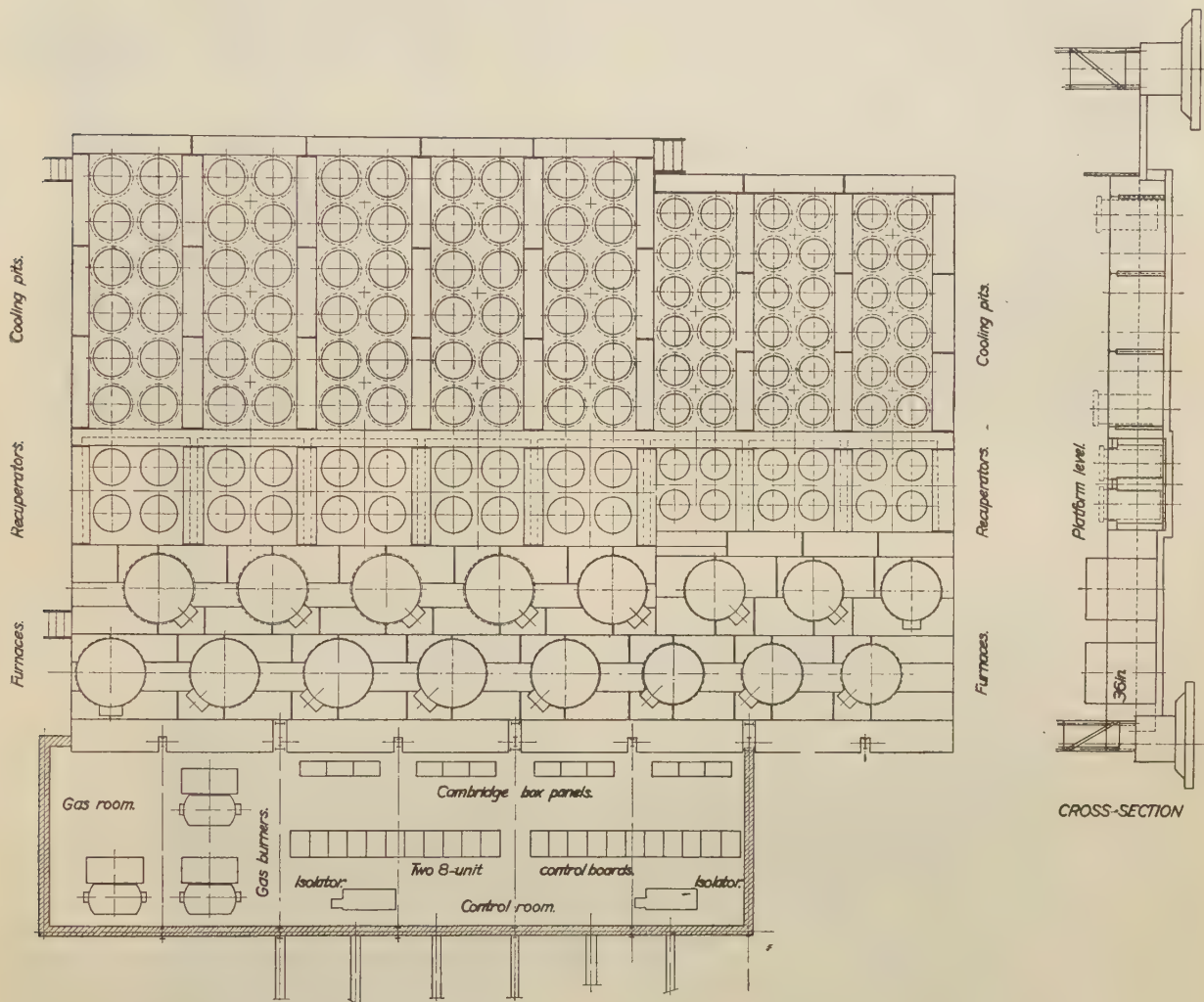


FIG. 1.—Schematic Layout of the Annealing Plant.

in Fig. 1, and a photograph of the plant, which was designed on the experience gained in the No. 5 bay annealing plant, is shown in Fig. 3. The floor space occupied by the plant is approximately 7,900 sq. ft. The installation is situated on a site adjacent to the electrical sub-station and near the cold-rolling mills in No. 6 bay.

Sixteen annealing furnaces are arranged in two staggered rows on concrete plinths, set just below floor level. Six furnaces are each rated at

recuperation and cooling pits. Each furnace is provided with two recuperation pits and six cooling pits, holding eight annealing pots, in all the total number of pits thus holding 128 pots. This arrangement ensures a continuous annealing cycle.

The plant is served by a 10-ton overhead crane for the loading and unloading of the pots. An electromagnet is used for the transport of the coils of strip to a site adjacent to the plant for loading

on to the base-plate, and for discharging the coils after annealing.

There are three gas burners for the production of the controlled atmosphere, each having an output of 1000 cu. ft. of burnt gas per hour. The burners are located in an alcove on the platform at the end of the line of furnaces, as shown in Figs. 1 and 3, and are referred to later. The annealing gas is connected to a "Mono" CO₂ recorder, which gives a well-defined and continuous indication of the CO₂ content of the gas from the common gas main, this being a sufficient guide to gas composition. The recorder is situated near the gas burners, and is connected to four pipe-lines of small diameter, one to each burner for individual tests on the gas when required, and one to a common gas main from the burners in operation.

The temperature-control cabinets and all the electrical switch-gear are situated at the rear of the furnace platform, as shown in Figs. 1 and 3.

Electrical Supply and Control.

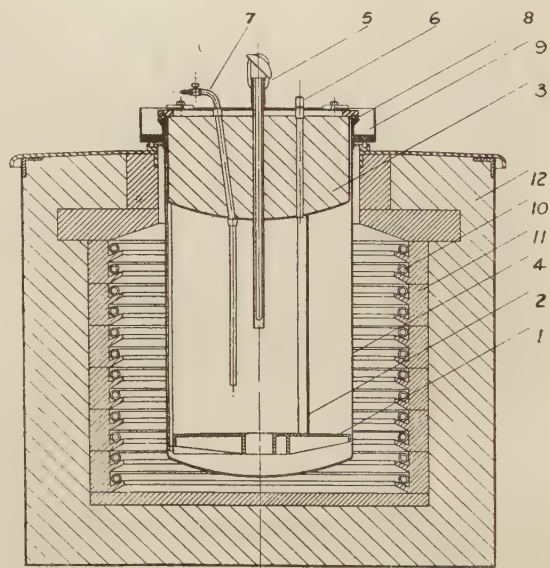
The plant is equally divided into two groups of furnaces, each group being supplied by a 6-kV. feeder from the adjacent sub-station. Each group is supplied by three 400-kVA. transformers, arranged in parallel *via* oil-immersed isolators to the 6-kV. feeders and connected on the low-voltage side, *via* air break isolators and oil-immersed circuit breakers, to a common bus-bar, from which the furnaces receive the supply at 400 V., 3-phase, 50 cycles. The high-voltage circuit breakers, of 250 MVA.* rupturing capacity, are fitted with inverse time-limit, overcurrent, and instantaneous earth-fault protection relays. The low-voltage isolators and circuit breakers for each group are mounted centrally on an ironclad board, with the main control gear on either side.

The first group consists of eight furnaces, Nos. 1-8, each taking coils of 44-in. dia. and rated at 130 kW., with a total maximum loading of 1040 kW. The second group of furnaces, Nos. 9-16, includes two furnaces taking 44-in. coils and six furnaces taking 36-in. coils, the latter being rated at 120 kW. each, giving a total maximum loading for the group of 980 kW. The root-mean-square value of the load is such that all the furnaces may be maintained in production in the event of a transformer failure. Each furnace has a separate cubicle containing a triple-pole isolator and link, backed by three fuses of high rupturing capacity. The cubicles also contain magnetically operated contactors which control the furnace elements, various coil fuses, and terminal strips required for the installation.

There are four temperature-control panels for the sixteen furnaces, as shown in Figs. 3 and 4. Each panel contains temperature controllers for four furnaces, and two-point thread recorders on

which the heating cycles of the steel charges in the four furnaces are continuously indicated. Each furnace is provided with three pilot lamps on the panel and, in order to prevent a variable ambient temperature around the cold junction of the thermocouples, the lamps are accommodated, together with the control switches, in an adjacent cabinet.

The heating elements are composed of heavy-gauge Nichrome wire, of $\frac{3}{8}$ -in. dia., in coil form, placed circumferentially around the inside wall of the furnace in suitably grooved refractory material, as shown in Figs. 2 and 7. The elements



- | | |
|------------------------------------|------------------------|
| 1. Base casting. | 7. Gas inlet. |
| 2. Heat-resisting suspension bars. | 8. Rubber ring seal. |
| 3. Thermally-insulated pot head. | 9. Water trough. |
| 4. Cylindrical annealing pot. | 10. Heating elements |
| 5. Pyrometer. | 11. Refractory lining. |
| 6. Non-return valve or gas outlet. | 12. Thermal insulation |

FIG. 2.—Diagrammatic Section through Annealing Furnace and Pot.

are arranged in two circuits, with alternate coils in each circuit. One circuit, *i.e.*, one-half of the elements, is arranged to cut out at a temperature 10° C. below the set furnace temperature, thus reducing the power input—and consequently reducing the rate of heating—as the required temperature is approached. The remaining circuit is switched off on attaining the maximum required temperature. As a result, temperature control is assured, and a uniform heat is obtained in a vertical plane within the charge.

The tip of the controlling furnace pyrometer (Chromel-Alumel) is exposed, as illustrated in Fig. 7. The position of the hot junction is important, and it must be placed in the source of

* Megavolt-amperes.



FIG. 3.—General View of the Plant.



FIG. 4.—Annealing Furnace and Temperature-Control Panels.

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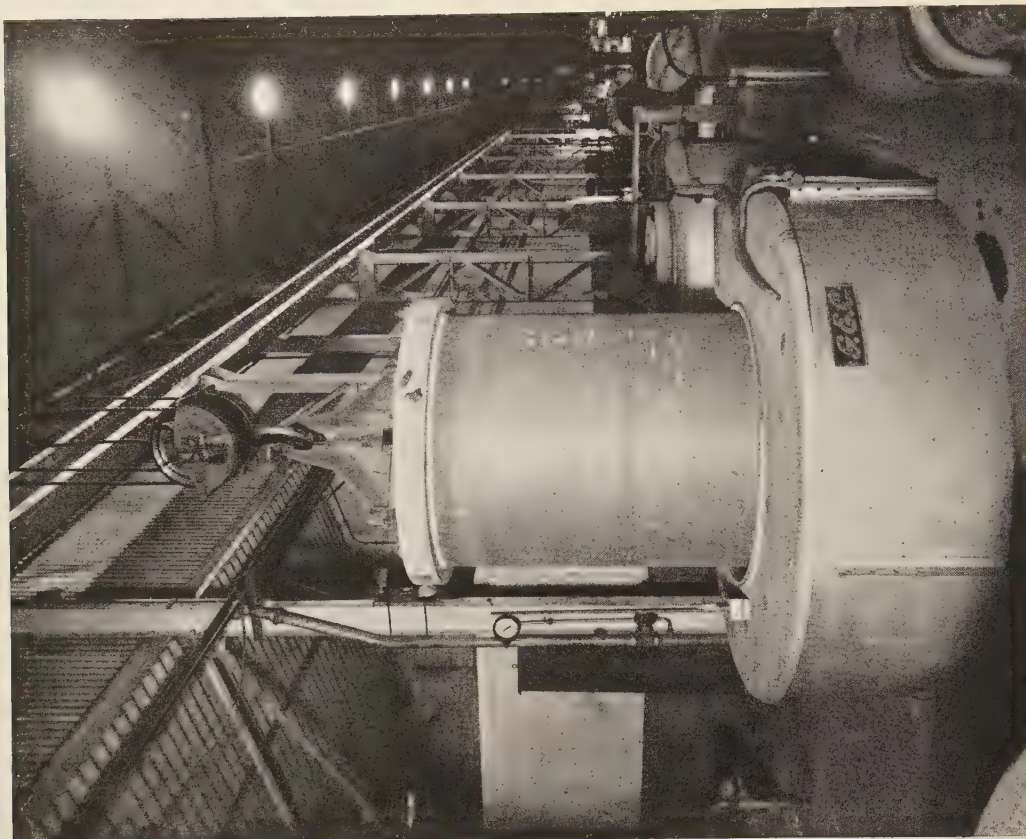


FIG. 6.—Annealing Pot being Lowered into Furnace.

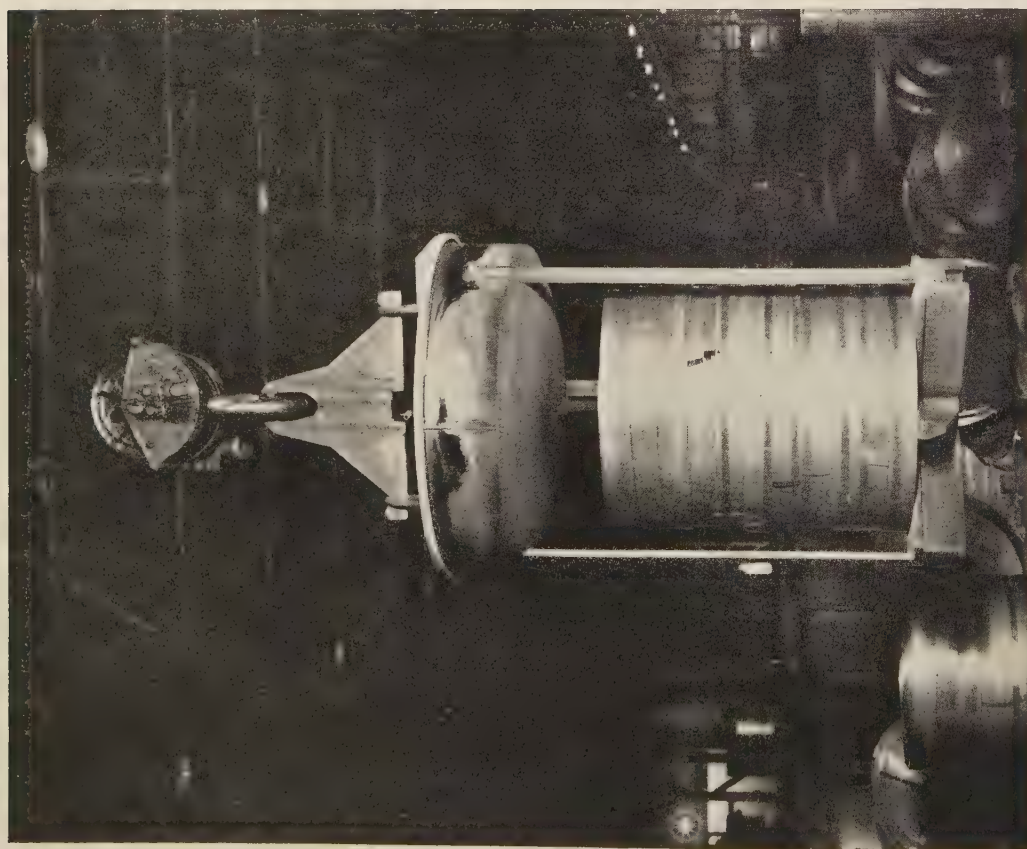
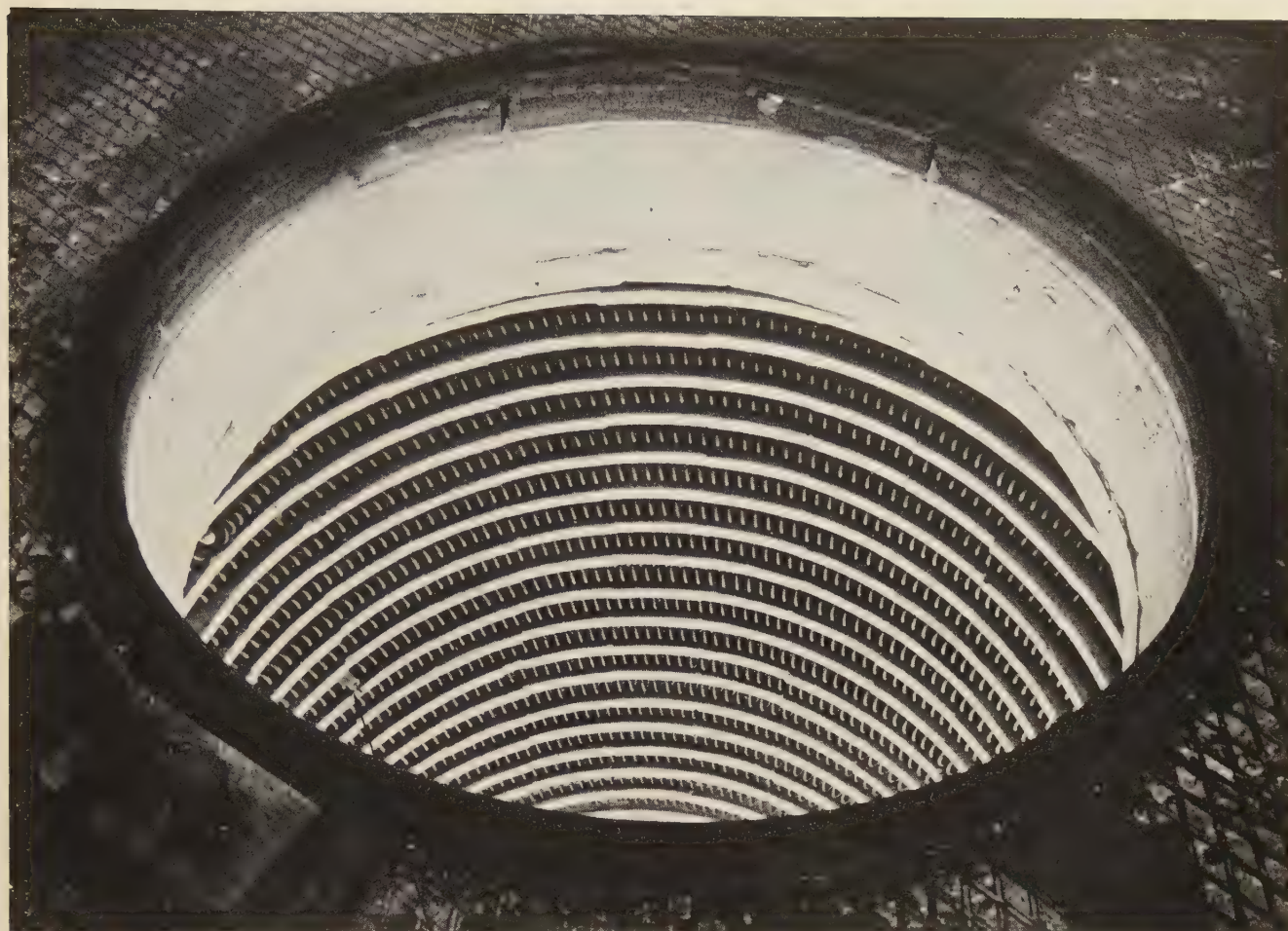


FIG. 5.—Coils of Steel Strip Mounted on Base-Plate after Bright Annealing



Thermo-couple.

FIG. 7.—Interior of Annealing Furnace, showing heating elements, controlling pyrometer, and pot switch.



FIG. 8.—“Selas” Air and Gas Proportioning Valve.

[Jones and Jenkins.]

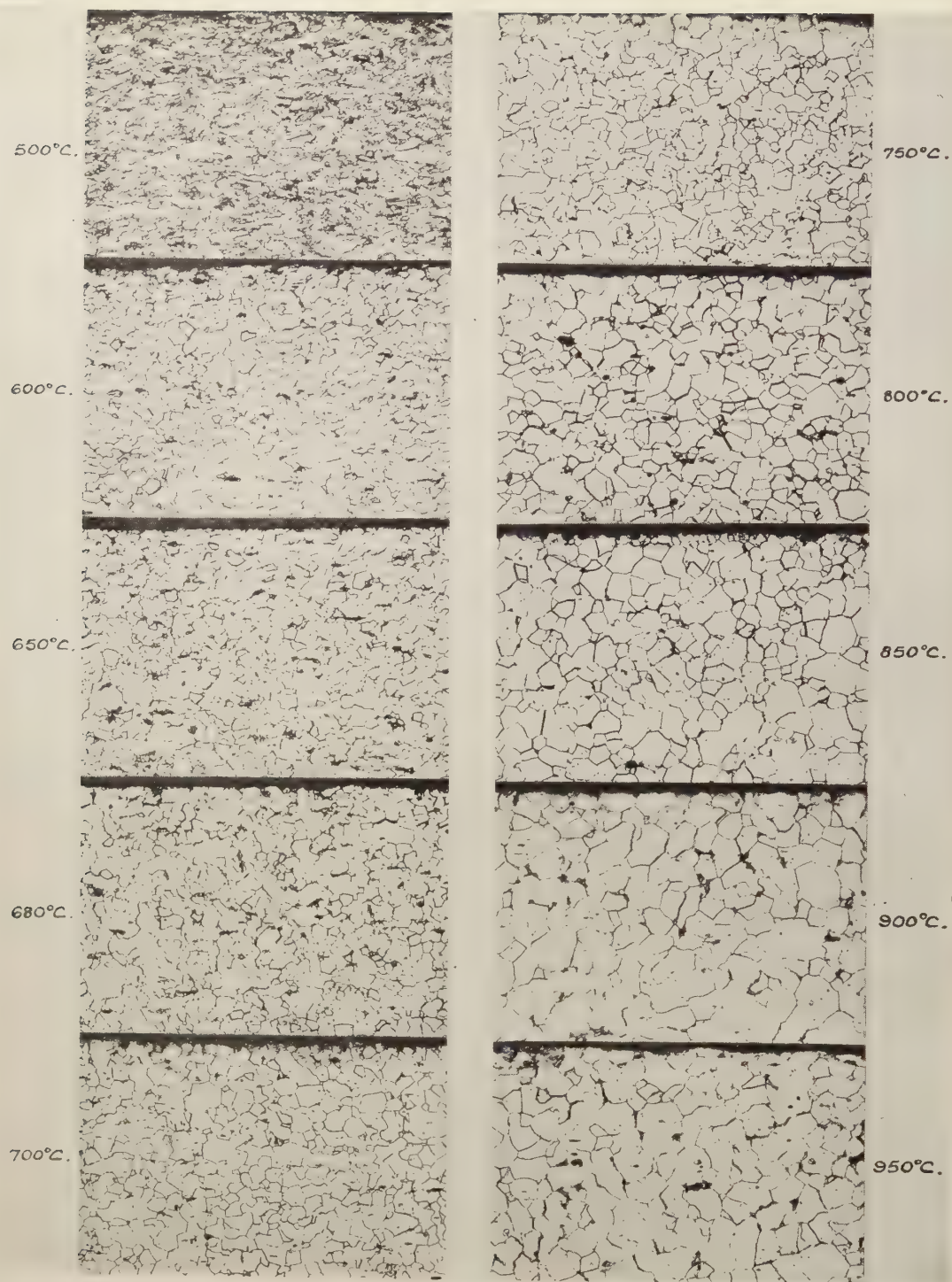


FIG. 9.—Steel EV (0.04% of carbon), cold-reduced 55% and annealed. $\times 100$. (Reduced to four-fifths linear in reproduction.)

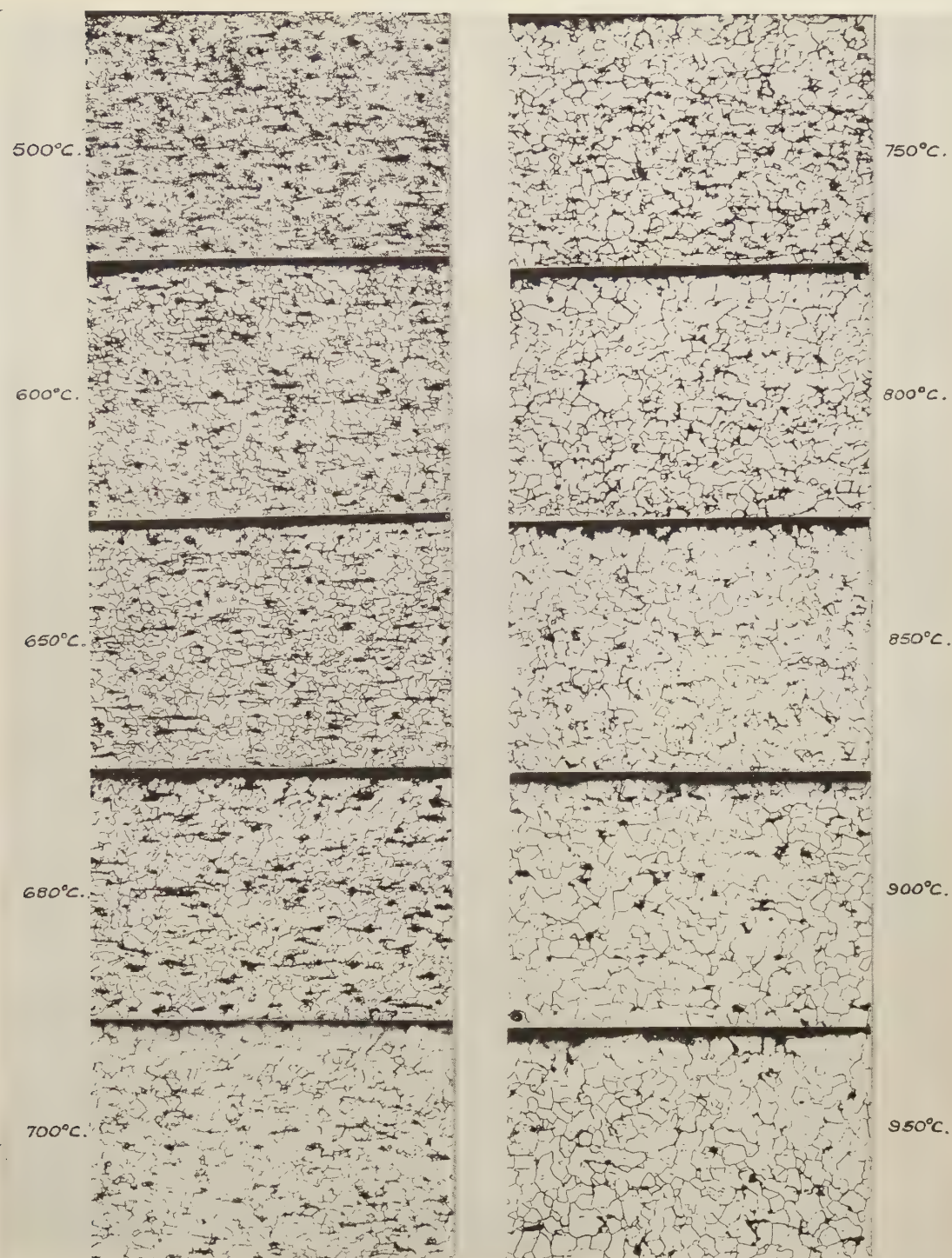


FIG. 10.—Steel RT (0.09% of carbon), cold-reduced 55% and annealed. $\times 100$. (Reduced to four-fifths linear in reproduction.)

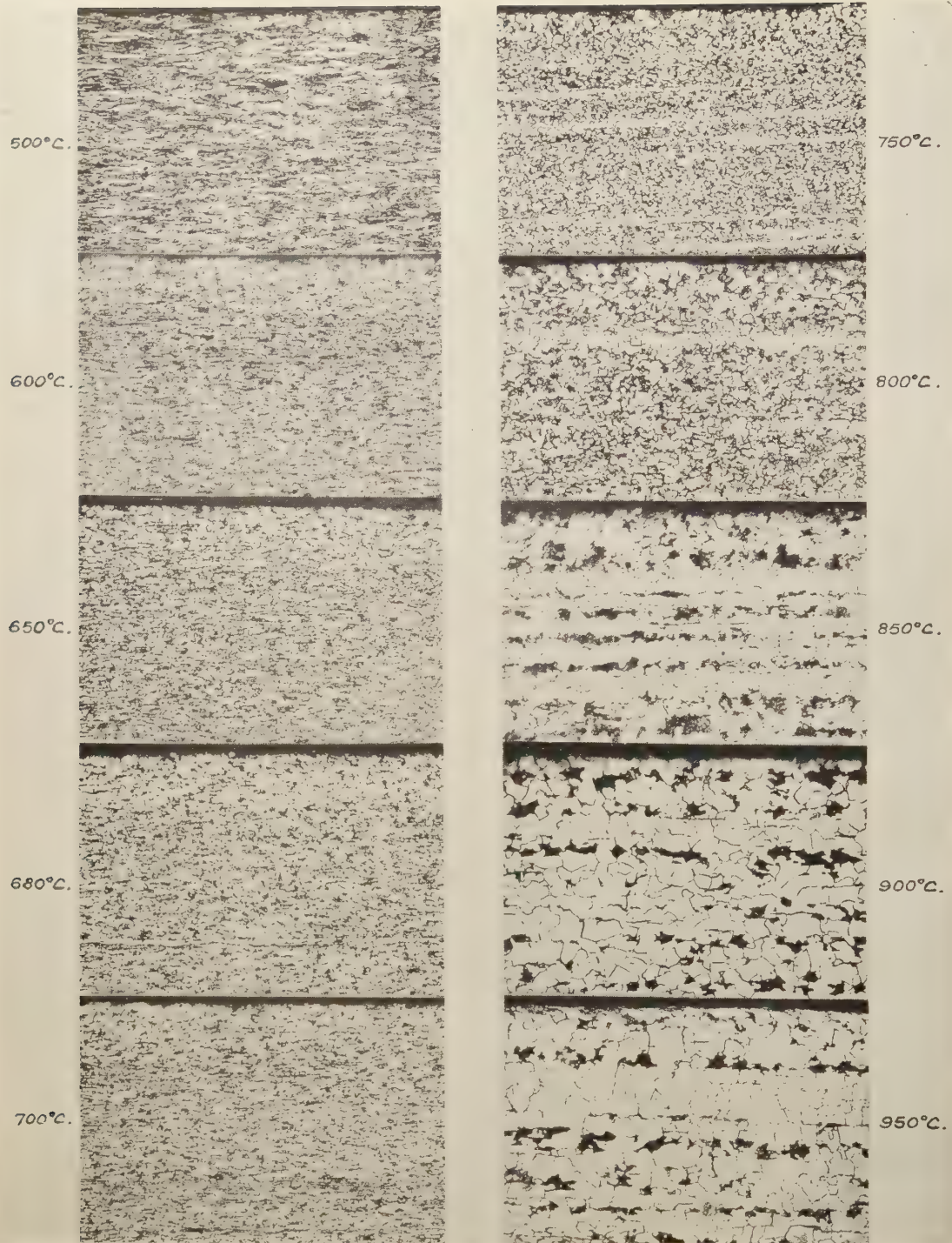


FIG. 11.—Steel W (0.18% of carbon), cold-reduced 55% and annealed. $\times 100$. (Reduced to four-fifths linear in reproduction.)

[Jones and Jenkins.
[To face p. 167 P.

maximum radiated heat. The couple passes through the furnace wall so that the tip is placed immediately above one of the elements in the centre of the furnace, at a position midway between the elements and the annealing pot. This arrangement ensures that the pyrometer is in the position of maximum temperature in the furnace, and prevents the overheating of the annealing container and the steel charge. Typical records of the furnace and charge temperatures are shown in Figs. 14 and 15, and are referred to later. Excess-temperature fuses of gold are located in each circuit of the furnace elements, thus safeguarding against overheating in the event of a failure in the temperature-controlling circuit. The fuses are connected in series with a specially designed safety switch fitted to the top of the furnace. The safety switch ensures that the furnace current is switched off when the annealing pot is withdrawn from the furnace, the heating-circuit switch being depressed by an attachment to the annealing pot. A cast-iron bracket carrying the safety switch is extended to accommodate a substantial earthing contact, which efficiently earths the charge and the furnace during the heating cycle.

The Charge and Annealing Pots.

The main features of the annealing container and the furnace are shown diagrammatically in Fig. 2. The charge of steel for annealing, in the form of coils of strip, is assembled on a star-shaped base casting of heat-resisting cast iron, suspended from an insulated pot-head by means of three heat-resisting suspension bars, as shown in Fig. 5. The whole is lowered into a lightweight envelope of heat-resisting steel, forming the annealing container, and the pot-head is clamped on to a rubber ring fitted to the top of the annealing pot. The rubber-ring seating, which ensures a gas-tight seal, is kept cool by a channel water-seal around the top of the pot, through which water circulates. The cost of the cooling water is negligible, as it is re-circulated after cooling. Inlet and outlet pipes for the controlled atmosphere pass through the insulated pot-head, the inlet pipe being extended centrally through the stack of coils to the base-plate. The Chromel-Alumel pyrometer for indicating the charge temperature is enclosed in a heat-resisting tube passing centrally through the pot-head to a position half-way down the stack of coils. All the fittings are welded to the inner covering of the pot-head to ensure gas tightness. A close-up of an annealing pot entering a furnace is shown in Fig. 6.

The main feature of the annealing container is that the total weight of the charge is carried by the three suspension bars, thus permitting the use of an outer envelope of light construction, which arrangement promotes a more rapid transfer of

heat from the furnace to the pot, and hence to the steel charge. The suspension bars are $59\frac{1}{2}$ -in. in length between the feet, and are $2\frac{3}{8}$ -in. wide \times $\frac{15}{8}$ -in. thick for the heaviest charge and, as these must support the weight at the annealing temperature, the selection of suitable heat-resisting material, possessing adequate tensile strength and a high creep resistance at the maximum temperature attained, is important. Experience obtained on the original electric annealing plant showed that the austenitic heat-resisting steel bars were subject to intercrystalline cracking and creep, this being particularly noticeable in wrought bars of welded construction. In some cases the bars extended gradually during service by as much as 3 in. on a bar 62-in. in length, extension being particularly severe at furnace temperatures above 800° C. Premature fracture of the suspension bars would result in damage to the bottom of the pot by the collapse of the charge. Cast bars of nickel-chromium alloy (Cronite) have given exceptionally good service, especially for the heavier charge weights, owing to the high tensile strength and creep-resisting properties of the alloy at temperatures up to 900° C. The bars are retained in sets for each annealing container to avoid using any of irregular dimensions.

The larger size of annealing container has an effective loading space of 44-in. dia. \times 48-in. deep, and is designed to take a maximum charge weight of 4.5 tons. The equivalent charge weight for the smaller container is 3 tons for a loading space of 36-in. dia. \times 48-in. deep.

The Recuperator.

A considerable economy in annealing costs is effected by utilizing the heat content of the pots discharged from the annealing furnace to preheat the freshly loaded containers before charging these into the furnace. Brick-lined recuperator pits, shown in Figs. 1 and 3, immediately in front of the furnace and situated between the latter and the cooling pits, are provided for this purpose. Each recuperator contains four annealing pots and is served by two furnaces, so that when working to capacity, the recuperator holds two pots cooling down and two cold pots being heated up before annealing, the hot pots from the furnace being placed diagonally opposite each other. The efficiency of recuperation depends on the continuous operation of the furnaces associated with the recuperator. When working at maximum production from the plant, the temperature attained at the centre of the pot before charging into the furnace is 225–250° C. The average temperature of the steel charge is higher than this, owing to the increasing temperature towards the pot envelope, but, assuming an average preheat temperature of 250° C., this represents a saving in

power consumption of 35–40 units per ton of steel treated. Furthermore, it has been found to be advantageous to preheat the charge from the standpoint of preserving a bright surface, apart from any saving of heat.

The Controlled Atmosphere.

The gaseous atmosphere used for bright-annealing is partially burnt town's gas, which is derived from three gas burners, each having an output of 1000 cu. ft. of burnt gas per hour. Two burners are in use, one being maintained as a

vertical sliding action opens or closes the gas and air inlet ports, thus admitting definite air/gas ratios. Adjustments for different proportions of gas and air are made by turning the hand-wheel of a vernier device, according to whether more gas and less air, or *vice versa*, are required, a pointer on the scale indicating the area ratios of the gas and air inlet ports of the proportioning valve. The compressor raises the mixture to the required pressure (10–84 in. W.G.) for the burners. When the supply from the apparatus is in excess of the demand at the burners (following,

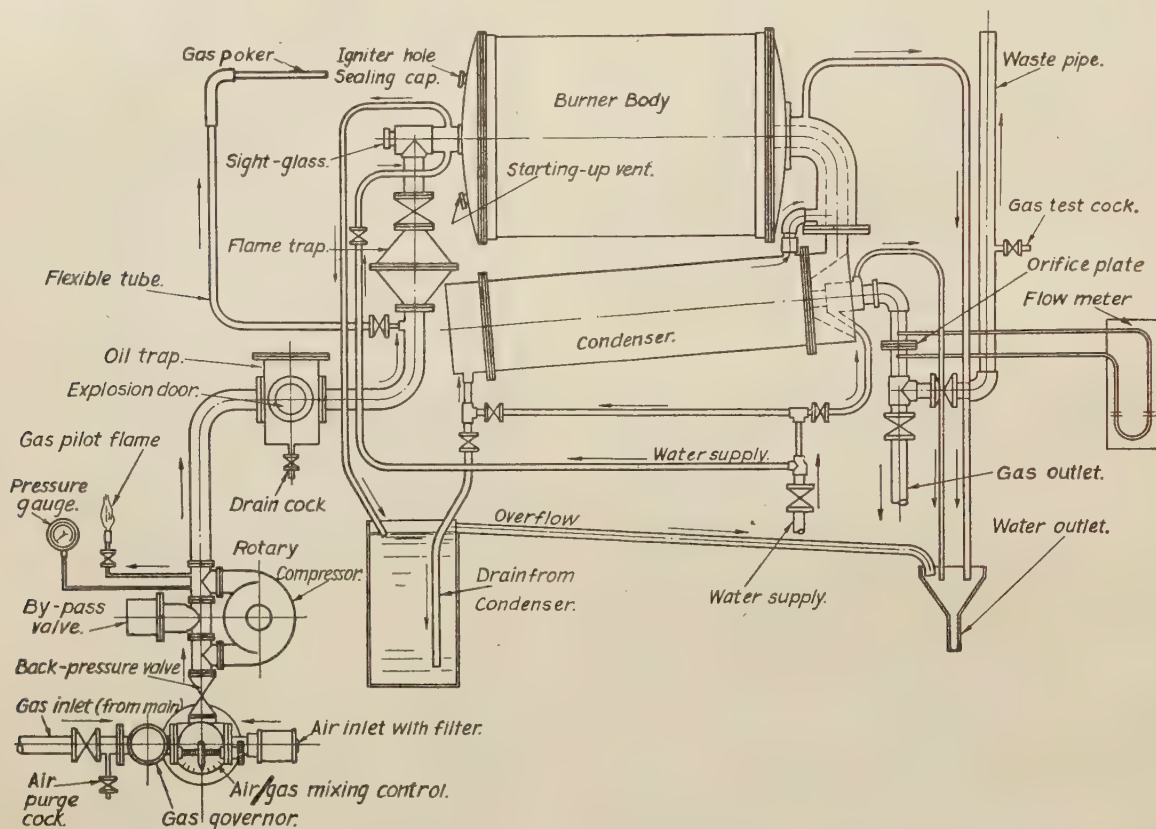


FIG. 12.—Schematic Arrangement of a Controlled Atmosphere Generator.

spare. Each unit is self-contained, compact, and of simple construction. A schematic arrangement of a gas burner is given in Fig. 12.

The regulated amounts of town's gas and air are supplied to the combustion chamber by a "Selas" automatic gas and air mixing apparatus, shown in Fig. 8. The gas supply is reduced to atmospheric pressure by means of a governor situated at the gas inlet of the mixing valve. Air is passed through a filter, and is directly induced at the opposite side of the proportioning valve. The mixture has a common outlet, the valve being operated by the suction or back-pressure created by a rotary compressor. The valve rises or falls over a certain distance and its

for instance, a reduced output from the furnaces), the by-pass valve of the pressure controller opens and connects the outlet of the compressor with its inlet. This causes the back-pressure valve to close, cutting off the air/gas supply from the proportioning valve to the compressor until the demand is stabilized. The test burner at the compressor outlet indicates by the height of the inner cone of its flame, the approximate proportions of gas and air contained in the mixture.

Ignition of the air/gas mixture on starting-up the plant is by means of a gas poker, and a heat-resisting sight-glass fitted behind the burner nozzle provides a means of viewing the combustion conditions inside the chamber.

From the compressor, the gas mixture passes through an oil filter and flame trap to a cylindrical combustion chamber. The flame trap safeguards the "Selas" unit against possible damage should the flame at the burner nozzle strike back down the mixture supply line. The combustion chamber is packed with perforated refractory discs which fill the cross-section along a length of 14-16 in. The packing material provides a hot, refractory, and catalytic surface on which the burnt gases react, to ensure a complete removal of free oxygen, a reduction of hydrocarbons to a minimum, and chemical equilibrium in the gases themselves. The gas burner operates within a certain range of temperature, usually 1150-1250°C. and, since

and water vapour against those of carbon monoxide and hydrogen respectively, in order to prevent oxidation of the iron at any stage during the annealing treatment. Typical compositions of annealing gases are as follows :

	CO ₂ , %.	CO, %.	H ₂ , %.	CH ₄ , %.	N ₂ , %.
(a) .	4.0	11.6	14.8	0.7	68.9
(b) .	3.3	10.0	14.5	0.3	71.9
(c) .	4.5	9.8	15.6	0.9	69.2

A suitable range of composition is obtained by adjusting the air/gas ratio in the proportioning valve to give a reading within the range of 3-6% on the CO₂ recorder. The concentration of methane in the burnt gas is normally so low in comparison with the volume of other gases present that it has no effect on the surface of the steel strip. Sulphurous gases are present in the annealing gas, but as the total sulphur content is low (less than 5 grains/100 cu. ft.), it has no deleterious effect on the bright-annealing process, nor on the material of which the annealing container is composed. Desulphurization of the furnace atmosphere is, therefore, unnecessary.

The hot products of combustion are cooled to approximately 20°C. to remove the excess of water vapour, formed during the combustion process, by passing through a tubular surface-type cooler. The amount of water vapour above the saturation value for this temperature (2.3%) is condensed and automatically drained away. The cooled gas returns through a central pipe in the cooler, and passes through an orifice plate connected to a calibrated flow-gauge, which indicates the output of the unit in cubic feet of burnt gas per hour. The burnt gas passes into a common main, and thence to the furnace plant.

During the cooling period the staining of the strip resulting from various surface reactions, such as oxidation by water vapour, or sooting by the decomposition of carbon monoxide, is prevented by cooling the annealing pots under pressure of gas. As the volumes of air and gas flowing through orifices or ports of given areas in the "Selas" mixer are dependent upon specific gravities, it is obvious that the best results are obtained when using town's gas of a constant composition. Trouble has been experienced when using an emergency supply of a mixture of variable proportions of water gas and coke-oven gas, when it was difficult to retain the composition of the burnt gas within fixed limits. This was due to the higher specific gravity of water gas, and its greater C_nH_m content. If the ratio of air to gas is less than 2:1, by reason of a change in composition of the raw gas, the methane content of the burnt gas may be sufficiently increased to cause sooting of the steel surfaces by its decomposition. The reverse conditions are obtained if the CO₂ content is above 6%, when blueing of the charge occurs by

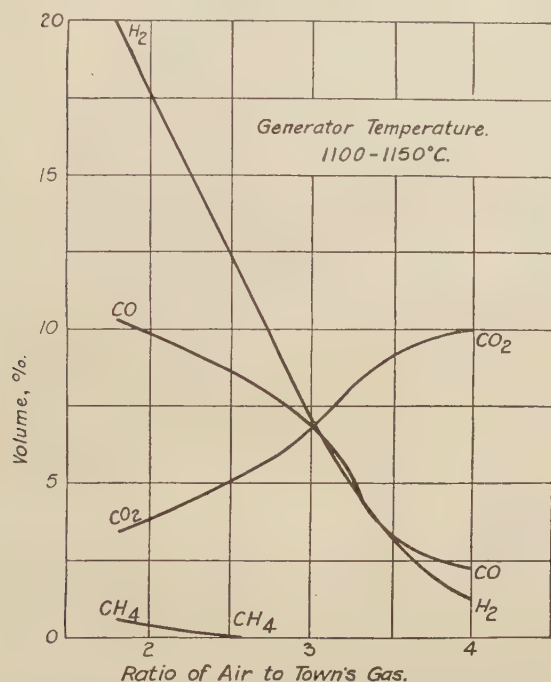


FIG. 13.—Composition of Burnt Town's Gas.

the calorific value of town's gas is approximately 500 B.Th.U./cu. ft., this range of temperature corresponds to a definite input of gas. The volume of air required for combustion will vary with the composition of the town's gas, but the ratio of air to town's gas used for the annealing of low-carbon steel is generally 2:1, and the volume of the cooled burnt gases is approximately equal to the volume of air used for combustion.

The composition of the burnt gas obtained by varying the proportion of air to town's gas is given in Fig. 13. The partially burnt gas delivered to the annealing furnaces contains carbon dioxide, carbon monoxide, hydrogen, water vapour, a little methane, sulphurous gases, and nitrogen. For the bright-annealing of steel, it is necessary to balance the concentrations of carbon dioxide

oxidation. Complete analyses of the controlled atmosphere are made at intervals for control purposes.

The burnt town's gas is fed to all the necessary supply points at the furnaces, recuperators, and cooling pits, through pipe-lines running in ducts set just below the level of the working platform. All the secondary gas lines have a slight inclination downwards to an open U-tube seal at the extreme ends, in order to avoid stoppages in the pipe-lines resulting from water condensation from the annealing gas. The ducts also carry water supply lines to the ring seals on the annealing containers, the furnaces, and the recuperator pits, together with water drains.

Surface Finish.

"Sticking" of the coils is practically unknown by annealing in a controlled gas atmosphere, whereas it was a periodic feature in the old method of annealing.

The charge as a whole is uniformly bright-annealed, and the original cold-rolled surface is preserved. Rolling oils may influence the quality of the surface, in that these provide, by evaporation, concentrations of heavy hydrocarbon vapours which may dissociate and produce surface deposits on the steel, which is an active catalyst for the pyrolysis of such vapours.* Mineral and rape oils do not present much difficulty, but heavy oils and complex soluble oils are prone to cause staining of this nature. Good results are obtained on the steel strip rolled with a soluble mineral-oil lubricant. The excess of the oil is removed by pads bearing on the strip as it leaves the finishing stand, and the surface is afterwards coated with a film of special-grade mineral oil before coiling on the reel. There is a minimum amount of oil retained on the strip after re-coiling in the slitting machines before annealing. This method gives a better protection during the interval between rolling and annealing than does that obtained from the presence of soluble oil alone. The latter is apt to cause the formation of dry patches containing oxide corrosion products, which give rise to a pronounced sooting of the annealed material. This may be due to the fact that the local rusting of the steel, followed by reduction in the annealing gas, provides active spots of iron, which catalyse the dissociation of the oil vapours. On the other hand, the oxidized oil has probably a higher boiling point than the original oil, so that the steel is at a higher temperature when the oil is evaporated, thereby promoting the breakdown of the hydrocarbons. Many attempts have been made to eliminate "oil-staining" in the coils, but it became obvious that the only solution was to drive out the oil vapours from the container as quickly as these were formed.

The slowing down of the initial rate of heating, brought about by switching off the furnace, allows an effective removal of the oil vapours from the pot before the charge has attained a temperature sufficiently high to promote the rapid breakdown of the hydrocarbons. It is not necessary to clean the strip free of oil before annealing.

The Annealing Cycle.

The charge of steel strip in the form of coils is stacked on the base support by means of an electromagnet, and the whole is attached firmly to the head of the annealing pot by the three suspension bars. The loaded pot-head is transferred by an overhead crane to the pot located in one of the cooling pits and the head is clamped down on to the rubber-ring seal on the pot itself. In due course the pot is transferred to a recuperator pit when one becomes vacant, and it remains there for a length of time determined by the heating cycle of the charge already in the furnace. This time varies according to the wall thickness of the coils and the weight of the charge, some typical figures being 12 hr. for a charge of $4\frac{1}{2}$ tons and 9 hr. for a charge of 3 tons. The average temperature attained during recuperation, as previously stated, is normally 225–250° C., and, during the preheating, the annealing gas is passed through the pot at a flow of approximately 30 cu. ft./hr., this rate of flow being sufficient to ensure complete purging by the end of the recuperation period.

The pot is transferred from the recuperator pit to the furnace, the necessary connections are immediately made to the controlled atmosphere and the water supplies, and the charge pyrometer is positioned through the head of the pot. These operations normally take 2–3 minutes. The flow of gas to the annealing pot is increased to approximately 50 cu. ft./hr., and this rate of flow is maintained throughout the period during which the pot is in the furnace. In order to reduce the possibility of the cracking of the oil vapours, due to a rapid initial rate of heating of the outside coils, it is the usual practice to cut off the electrical supply to the furnace for the first hour. The rate of heating during this period is thus slowed down, and the oil vapours are quickly swept out of the pot by the gas at a temperature too low to induce any appreciable cracking on the steel surfaces. After 1 hr., the current is switched on, and the furnace is controlled at the required temperature within the range of 750–800° C. for sub-critical annealing, the rate of heating depending on the size of the coils. When the charge pyrometer located inside the stack of coils attains the required annealing temperature, the furnace current is switched off, and the charge is allowed to soak for approximately 1 hr., to allow

* I. Jenkins and S. V. Williams, *G.E.C. Journal*, 1942, vol. 12, No. 1, pp. 38–50.

the heat to diffuse as uniformly as possible through the coils. At the end of this period, the gas outlet on the pot-head is effectively sealed by the screw-down non-return valve, and with the inlet pipe still connected to the controlled atmosphere by means of a flexible hose, the pot is transferred to a recuperator pit, where it remains until it has cooled to a temperature of 350 to 400° C., when it is withdrawn and taken to a cooling pit. Throughout the cooling stage the gas inlet pipe remains connected to the controlled atmosphere supply, the pot drawing in sufficient

discussed in the Appendix. Thus, whilst the charge as a whole approaches closely to a uniform temperature during the last stages of the annealing cycle, the outside portion of the charge has previously attained a somewhat higher temperature for some time. The mechanical properties of the steel from various parts of the coil are similar, however, as shown in Table I.; the bend tests were satisfactory at 180° flat in all annealed specimens, in longitudinal and transverse directions. Temperature uniformity can be obtained more closely when required, by prolonging the time of annealing

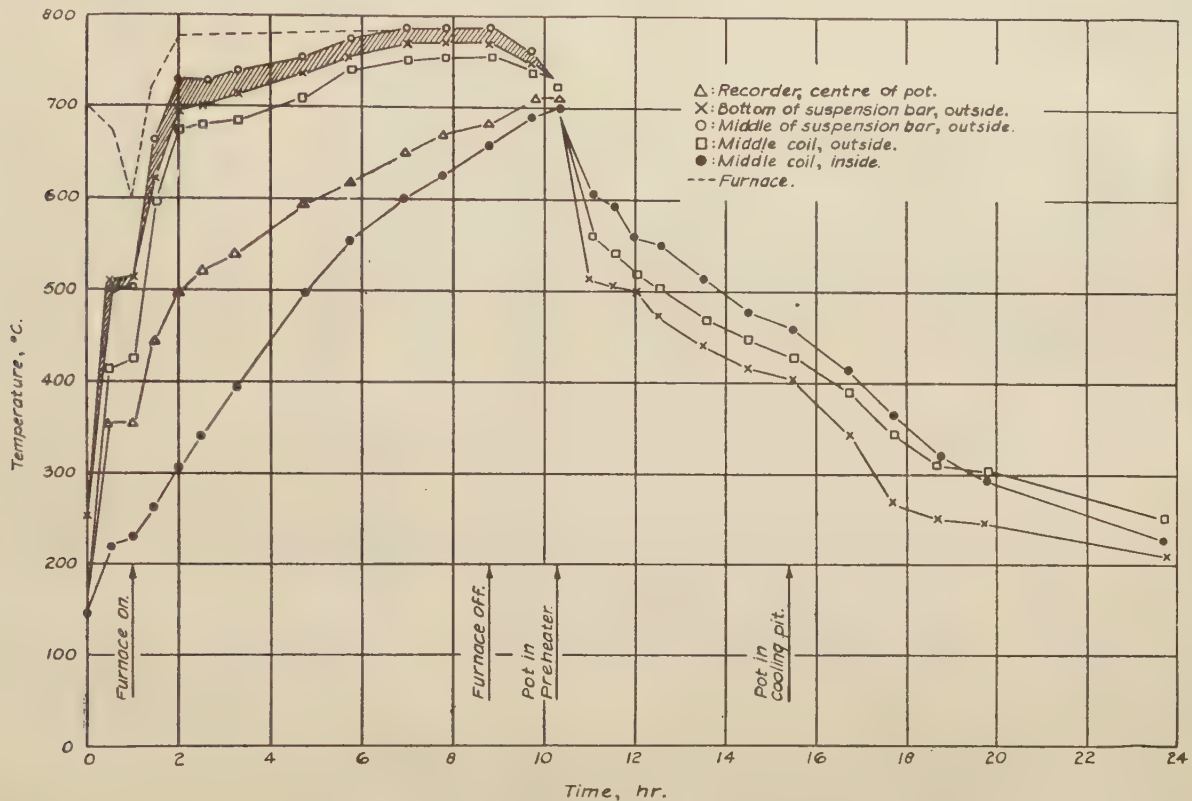


FIG. 14.—Heating and Cooling Curves for 3½-Ton Charge of Steel Strip.

gas to compensate for the reduction in pressure due to cooling.

A typical heating and cooling curve, showing the temperature distribution in the furnace and at various parts within the pot, is shown in Fig. 14. The outside of the steel charge gradually increases in temperature to within 40° C. of the controlling furnace temperature and is maintained at this temperature until the current is switched off. The inside of the coils are raised more gradually in temperature, as heat transfer through the wall of the coil is mainly by thermal conduction and, to a lesser extent, by convection by the circulating atmosphere. There is a certain range of annealing temperature, however, in which the deep-drawing properties are attained in mild steel; this is

and by adjusting the furnace temperature during the cycle. This is illustrated in Fig. 15, which gives the heating curve of a charge of 3¼ tons of steel strip which has been annealed uniformly within the temperature range of 694–699° C. in 15 hr. With charges of standard weight and coil dimensions, no difficulty is experienced in following definite annealing schedules, and thereby annealing the charge within the required temperature limits. Tests have shown that there is a similar close temperature control from top to bottom of the charge.

Throughout the cooling period, a flow of gas through the annealing pot would tend to cause staining, by both oxidation and sooting, whereas cooling under pressure prevents this effect and

TABLE I.—*Properties of Mild-Steel Strip Annealed in Vertical Cylindrical Electric Furnaces.*

Steel.	Test-Piece.	Hardness.		Erichsen., mm.	Yield Stress, tons/sq. in.	Maximum Stress, tons/sq. in.	Elongation on 2 in., %.
		V.P.N.	Rockwell "B."				
Composition :	As hot-rolled.	105	60	...	15.2	21.5	38.7
C 0.04%	As cold-rolled.	216	96	4.2	...	38.8	2.0
Si trace	Annealed top coil, outside.	82	42	11.9	14.4	20.3	41.0
Mn 0.29%	" " centre.	85	44	11.3	14.5	20.8	40.9
S 0.024%	" " inside.	85	44	11.6	14.7	20.9	41.3
P 0.013%	Annealed middle coil, outside.	84	43	11.8	14.1	20.6	41.6
	" " centre.	85	44	11.3	14.3	20.8	40.6
Quality :	" " inside.	86	45	11.5	14.5	20.3	40.7
Deep-drawing	Annealed bottom coil, outside.	83	43	11.3	13.9	20.1	41.4
(3½-in. × 0.040-	" " centre.	84	43	11.2	14.0	20.1	41.2
in. as-annealed).	" " inside.	84	43	11.3	14.0	20.2	41.0
Composition :	As hot-rolled.	113	65	...	17.8	24.9	33.8
C 0.09%	As cold-rolled.	228	98	5.0	...	46.8	3.0
Si 0.05%	Annealed top coil, outside.	100	57	11.8	16.0	23.0	38.5
Mn 0.39%	" " centre.	100	58	11.6	16.1	23.4	37.5
S 0.033%	" " inside.	101	59	11.8	16.5	23.6	37.5
P 0.015%	Annealed middle coil, outside.	101	59	11.6	16.2	23.3	35.0
	" " centre.	102	59	11.2	16.4	23.5	35.0
Quality :	" " inside.	101	59	11.5	16.6	23.6	38.0
Cold-pressing	Annealed bottom coil, outside.	102	60	11.4	16.6	23.8	36.0
(2½-in. × 0.046-	" " centre.	103	60	11.2	16.4	23.7	35.0
in. as-annealed).	" " inside.	102	59	11.6	16.6	23.7	35.0

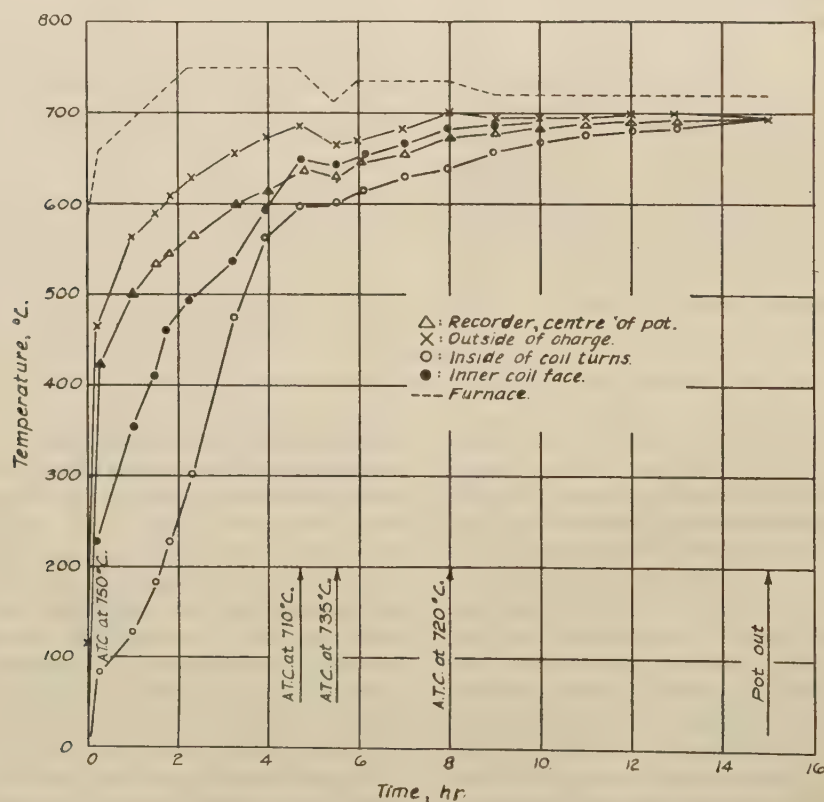


FIG. 15.—Heating Curve for Annealing within a Close Temperature Range.

retains a bright surface. Oxidation in a flow of gas would be caused by the presence of the water vapour in the gaseous atmosphere. The hydrogen content in the gas is about 15%, so that the ratio of water vapour to hydrogen corresponds to equilibrium for the reaction $\text{Fe} + \text{H}_2\text{O} = \text{FeO} + \text{H}_2$ at approximately 450° C. Thus, at any temperature below this, in a continuous stream of gas, the water vapour would give rise to oxidation of the steel, owing to the slow rate of cooling pertaining to batch annealing. Sooting of the steel would also occur by cooling in a flow of gas, by the breakdown of carbon monoxide (as shown by Jenkins and Williams, *loc. cit.*) according to the reaction $2\text{CO} = \text{CO}_2 + \text{C}$. The reaction proceeds very slowly, however, at temperatures below 600° C., unless it is catalyzed by an active metal surface. It is known that both iron and nickel promote the decomposition of carbon monoxide, especially in the temperature range of 500 to 300° C. The nature of the surface of the catalyst has a marked bearing on its activity, and in this respect a cold-rolled steel surface is far less reactive than one of reduced oxide particles. Soot deposits can build up, however, on slow cooling in batch annealing, so that precautions must necessarily be taken to restrict the volume of gas coming into contact with the steel charge. Whilst the decomposition of the carbon monoxide is promoted at temperatures up to approximately 600° C. during the heating of the charge, the rate of heating is too rapid for the reaction to occur to any extent.

In addition to the production of bright-annealed strip, the plant is also used for blue annealing. The two processes are identical in every respect, except for the cooling stage when, in the blueing process, the pot-head and charge are lifted slightly at a temperature of approximately 500° C., thus allowing air to enter the pot, when the whole is finally cooled with both vents open to the air.

Annealing Costs.

Although the capital cost of the electric annealing plant is high, this is offset by a very small maintenance cost, uniform working conditions, and the good quality of the annealed strip produced. The life of the annealing pots is indefinite, in that no apparent deterioration has occurred to date, after, in some cases, more than 12 years' service, whereas the pots used in the former gas-fired annealing plant had a comparatively short life of 1½–2 years, thus entailing higher maintenance costs. The labour charges are small, since the work involved is mainly the charging and discharging of the coils, the plant being operated by two annealers and a crane driver on each shift. The consumption of electricity for heating the furnaces is 180–200 units/ton of steel annealed,

varying according to the charge tonnage, whilst the cost of the controlled atmosphere averages between 3½d.–4d./ton of steel.

ACKNOWLEDGMENTS.

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APPENDIX.—*The Effect of Annealing Temperature on the Properties of Heavily Cold-Reduced Mild-Steel Strip.*

In the low-temperature annealing treatment of a thick mass of metal, such as coils of steel strip stacked in a steel container, it is necessary to operate the heating furnace at a higher temperature than that desired in the steel charge, in order to heat the whole of the steel to the annealing temperature in a reasonable time. Heat is transmitted from the outside of the coil to the inner wall mainly by thermal conduction, consequently the outer convolutions of the coils are heated to a temperature greater than that attained by those on the inside throughout the heating period, the temperature gradient through the body of the coil being reduced in the later stages of annealing. It is important, therefore, to maintain a uniform temperature in the furnace itself to avoid any appreciable variation in temperature within the charge, in order to avoid the production of annealed material of a varying grain-size. Reference has been made to the advantages of electric annealing in this respect, and in special cases it is necessary to prolong the heating time by working with a comparatively low furnace temperature, in order to restrict the temperature gradient to a minimum. In the case of mild steel, the annealing treatment cannot be carried out economically to such close limits in many plants with furnaces of large capacity, owing to the lengthy time of heating involved for heavy charges, which would entail a restricted output.

Tests have been made on certain low-carbon steels to show the effects of heavy cold-reduction and subsequent annealing at various temperatures from 400–950° C. Much work has been carried out on the annealing of low-carbon steel sheets after various degrees of cold rolling up to 100% elongation, by C. A. Edwards* and his collaborators, as described in their well-known publications.

* C. A. Edwards, *Journal of The Iron and Steel Institute*, 1924, No. I, p. 129 P; 1927, No. II, p. 245 P; 1928, No. II, p. 118 P; 1936, No. I, p. 95 P.

The following tests have been made on more severely cold-worked steels which were cold-reduced in a continuous strip mill at a high speed of rolling. Coils of hot-rolled strip of basic open-hearth quality were pickled and oiled, and cold-rolled. Three steels with carbon contents of 0.04, 0.09, and 0.18% were cold-reduced by 55% in thickness, and a further steel containing 0.04% of carbon was cold-reduced by 84%. Suitable lengths of the cold-reduced steels were annealed in a small electric furnace, under temperature control and in an atmosphere of partially burnt town's gas. The steels were heated slowly to the annealing temperature, held at this temperature for one hour, and slowly cooled.

For the present purpose, the hardness and Erichsen values were determined, and the microstructures were examined. The results are given in Tables II. to VI. and in Figs. 9 to 11. After cold reduction the steels were hardened to within the range 213–236 V.P.N. (96–99 Rockwell "B") and the hardness of all the steels increased slightly after annealing at 400° C. On annealing at temperatures from 450 to 550° C. the hardness gradually decreased, and at 600° C., most of the work-hardening effects from cold-rolling were removed, as shown by an appreciable fall in hardness, and also by good Erichsen values. Whilst the cold-rolled structure was still visible in the steels annealed at temperatures up

TABLE II.—*The Compositions of Mild Steels used in the Tests.*

Steel.	C, %.	Si, %.	Mn, %.	S, %.	P, %.
EV	0.04	trace	0.29	0.024	0.013
EV2	0.04	trace	0.23	0.047	0.014
RT	0.09	0.05	0.39	0.033	0.015
W	0.18	0.08	0.55	0.062	0.034

TABLE III.—*The Annealing of Mild Steels after Heavy Cold-Reduction; Steel EV, Cold-Reduced 55% in Thickness.*

Annealing Temp., ° C.	Hardness.		Erichsen (0.040 in. thick).
	V.P.N.	Rockwell "B."	
As cold-rolled	213	96	3.8
400	216	96	5.5
450	203	94	6.6
500	170	87	9.4
550	100	57	10.7
600	94	51	11.8
650	91	48	11.9
680	89	47	11.8
700	86	45	11.8
750	85	44	12.0
800	84	44	12.1
850	83	43	12.3
900	83	43	12.4
950	82	42	12.0

TABLE IV.—*The Annealing of Mild Steels after Heavy Cold-Reduction; Steel EV2, Cold-Reduced 84% in Thickness.*

Annealing Temp., ° C.	Hardness.		Erichsen (0.015 in. thick).
	V.P.N.	Rockwell "B."	
As cold-rolled	220	97	3.4
400	225	98	4.3
450	207	95	4.4
500	203	94	4.7
550	135	74	7.2
600	92	49	9.5
650	87	45	9.7
680	83	43	9.6
700	83	43	9.8
750	82	42	9.7
800	82	42	10.0
850	76	38	10.0
900	75	37	10.1
950	75	37	9.8

TABLE V.—*The Annealing of Mild Steels after Heavy Cold-Reduction; Steel RT, Cold-Reduced 55% in Thickness.*

Annealing Temp., ° C.	Hardness.		Erichsen (0.046 in. thick).
	V.P.N.	Rockwell "B."	
As cold-rolled	223	97	4.0
400	226	98	5.2
450	213	96	6.8
500	206	94	9.2
550	177	88	10.8
600	108	62	11.6
650	104	60	11.6
680	103	60	11.6
700	103	60	12.0
750	101	58	12.0
800	100	58	12.0
850	99	57	12.0
900	96	55	11.9
950	93	53	11.9

TABLE VI.—*The Annealing of Mild Steels after Heavy Cold-Reduction; Steel W, Cold-Reduced 55% in Thickness.*

Annealing Temp., ° C.	Hardness.		Erichsen (0.038 in. thick).
	V.P.N.	Rockwell "B."	
As cold-rolled	236	99	4.0
400	245	> 100	3.5
450	233	99	3.7
500	228	98	7.3
550	196	92	8.5
600	127	72	9.6
650	123	70	9.7
680	120	69	9.6
700	118	68	9.9
750	116	66	10.0
800	113	65	10.5
850	110	63	10.0
900	108	63	9.8
950	106	61	9.6

to 550° C., after annealing at 600° C. the ferrite grains had recrystallized with a fine equi-axed structure. The largest grain-size at this temperature was in the deep-drawing quality steel, *EV* (0.020 mm.), but the grain-size was extremely small in steel *W* (0.18% of carbon) and in *EV2*, which had been more severely cold-reduced (by 84%). The hardness decreased by only a further 5–7 V.P.N. units after annealing at temperatures of 650–680° C. in all the steels, and the grain-size remained practically similar to that found after annealing at 600° C., being 0.020–0.021 mm. in steel *EV* and 0.017–0.018 mm. in steel *RT*, whilst the Erichsen values were similar. Annealing at 700° C. caused a definite but small increase in grain-size in all the steels (0.024 mm. in *EV* and 0.021 mm. in *RT*), a more equi-axed structure, and a spheroidizing of the carbide. These changes were accompanied by only an inappreciable increase in Erichsen values. The hardness decreased slightly and progressively in the steels after annealing at higher temperatures up to 950° C., and the grain-size gradually increased. The average grain-size of the steels *EV* and *RT*, after 55% cold-reduction and annealing, was as shown in the next column.

The steel *EV2*, cold-reduced by 84%, recrystallized with a much finer grain-size than *EV* throughout the annealing range, particularly at

Annealing Temp. ° C.	Grain-size, mm.	
	Steel <i>EV</i> .	Steel <i>RT</i> .
600	0.020	0.017
650	0.020	0.017
680	0.021	0.018
700	0.024	0.021
750	0.024	0.022
800	0.028	0.025
850	0.034	0.027
900	0.042	0.028
950	0.043	0.030

temperatures up to 800° C., and had a grain-size of 0.030 mm. after annealing at 950° C. The steel *W*, with 0.18% of carbon, also retained a very fine grain-size after annealing at temperatures up to 800° C., but a marked grain-growth occurred on annealing at 850° C., and a banded structure was present, which was only partially removed on annealing at 950° C., after which the steel had a grain-size of 0.031 mm.

As regards deep-drawing and cold-forming properties, it is evident that in low-carbon steels heavily cold-reduced in a strip mill, there is a range of annealing temperatures above 600° C. in which the work-hardening effects are effectively removed, good Erichsen values are obtained, and a suitable grain-size can be imparted.

Acknowledgments are due to Mr. A. H. Pople for his assistance with the above annealing tests and in preparation of the photomicrographs.

DISCUSSION.

Mr. D. A. OLIVER (Messrs. William Jessop & Sons, Ltd.): I think that the Institute is very fortunate in having this practical account of what I should like to describe as a straightforward laboratory technique translated into a large-scale plant. These developments appear to have taken ten years and have been done in progressive stages, obviously with a very keen eye on economics and with the very high ideal that in the bulk handling of material the final product shall be as uniform as the small laboratory sample. In that respect we can regard this paper as an account of a plant of which we can be nationally proud. If this paper had come from Germany or from America a few years ago we should have heard considerable comment about our clever competitors in other countries. Now that it has occurred in the home country we want to recognize the real achievement.

Before making any comments on matters of detail I should like to ask the authors whether I am right in my estimation that the recuperator system effects a saving of approximately 20% in electrical energy. If so, that appears to me to be an excellent saving from waste-heat recovery, as it might be called. In that connection, I noted that the recuperator pit is dismissed as being brick-

lined. I should like to ask whether very special insulating bricks were used, and whether, in view of the large recovery of heat, special precautions are taken to spend on the recuperator insulation something proportional to the dividend which that saving of heat would obviously justify.

In that connection, in 1943 I saw some most interesting insulating material in the U.S.A., which was really exploded mica. That might be of interest to the authors if they are considering the problem afresh. I understand that the mica stands up very well to the higher-temperature working and has a very low diffusivity and excellent properties.

Coming now to the characteristics of this plant, I should like to emphasize a sentence which occurs under the heading "The Charge and Annealing Pots" where the authors say "The main feature of the annealing container is that the total weight of the charge is carried by the three suspension bars." This is, I think, a very unusual arrangement, in so far as a very heavy load at high temperature is carried by three somewhat slender and elegant bars. I found the description at the top of the right-hand column of that page a little difficult to follow; the tensile strength at tempera-

ture is normally very much greater than the safe stress to produce a tolerable amount of creep, and it would appear that up to about 5% creep strain could be tolerated in this plant.

It seems as though a rather invidious comparison is made between forged heat-resisting material and cast heat-resisting material. The issue must be that it depends firstly upon what you make the components, and secondly on the basic fact that usually the creep resistance of a cast material is greater than that of a forged material; but against that as an asset it is necessary to offset the vagaries of casting, which means that bars which are cast have usually a greater spread in production than bars which have less creep strength but which are much more uniform.

The remark is made that intercrystalline cracking and creep occurs, and I should like that elucidated a little, because normally in the mechanism of creep the pre-stage of failure is intercrystalline cracking. Have the authors anything special in mind there?

Bars of welded construction are apparently unsatisfactory. This, I gather, was an early plant, but I have personally known of other bars which have been welded, and I believe that some of the later plants of this general type, having wrought and welded heat-resisting bars, are now considered to be quite satisfactory.

The value of the paper would be improved if the composition of the actual Cronite bars used could be stated to correlate with the service data given. To have heat-resisting bars working under relatively high tensile stresses up to 900° C. is a severe service condition, and it is interesting to learn that some of the newer special steels are likely to find a field of application in cases of this sort.

I was a little mystified by the reference to base castings of heat-resisting cast iron, and I should like the authors to confirm that description. Do they really mean cast iron with heat-resisting additions such as chromium, or is that just a small error? The base castings operating at 800° C. are more likely to be something more highly alloyed.

The other part of the paper in which I was particularly interested is the section in which reference is made to the control of grain-size in the annealed final product. I think that this is a case where one is dealing with a product which can probably justify a greater fuel cost if one can achieve the uniformity desired. I think that the contention of the paper is well borne out in that respect.

I have looked through the paper carefully to ascertain whether aluminium in excess was added to these steels. I believe that our friends in the U.S.A., when they talk about deep-drawing qualities, work with an excess content of acid-soluble aluminium of about 0.03%. The value of

this record would be very definitely enhanced by a statement whether the steel tested was aluminium-free or aluminium-containing. The general inference is that it might be aluminium-free.

On the last page of the paper, one of the advantages of this controlled annealing is stated to be that it produces a more equiaxed structure and a spheroidizing of the carbide. Are we to gather from this that the rolling texture is more or less eliminated by this completely controlled annealing and that spheroidizing of the carbide is a necessity for good deep-drawing performance? I found this section of the paper completely factual; but I think that it would help if one or two of these points were clarified.

Mr. V. O. CUTTS (General Electric Co., Ltd.): I should like to congratulate the authors on this paper, which I think is capable of being very useful. I shall have to avoid any semblance of answering the previous speaker, having had something to do with this work, but I think that it may be of interest if I make a few comments on the developments which led up to the plant and process described in the paper.

The forerunner of this process was the Grüne-wald process. The main object of that was to get bright annealing without the introduction of an artificial gas atmosphere. This process depended very largely on an atmosphere within the pot which was obtained in the main by evaporation of the lubricant on the strip. During the cooling period, by means of an effective sealing device and non-return valve, a partial vacuum was built up. A number of quite good results were obtained, but we found that this method was altogether too promiscuous; the results depended on the kind of oil used on the strip, on the quantity of oil put on to it in the rolling process, and in some cases on the length of time during which the rolled strip was allowed to stand about the shop before going through the annealing process.

These conditions led us into a long series of researches on rolling lubricants. We compared the mineral oils, the vegetable oils, and so on. Not only did that lead to a good deal of research work, but even when we felt that we were getting somewhere we encountered difficulty. It was therefore deemed desirable to develop a process which would enable us to get rid of the volatilized lubricating oil as early in the annealing cycle as possible and to depend on an atmosphere of known composition, which we knew would give us the results required without staining, sooting, and so on. In other words, the object was to substitute known conditions and known factors for what were not always known and were sometimes very variable.

Incidentally, it is interesting to note that the very first gas-atmosphere equipment which was

used on a commercial scale under practical conditions for producing the atmosphere used in the first of the two plants referred to in the paper, was the very first prototype built for experimental development work in the laboratory. There was no time to do anything else.

The point that I want to make is that, although the Grünwald process was a stepping-off ground, the features of the process as it is known to-day are entirely different from what they were in the days of the Grünwald process. There are some features of the old Grünwald process which are common to both, but there has been a tremendous amount of development even where those things are concerned.

The next point that you will notice in the paper is that the first gas-atmosphere producer had a capacity of 300 cu. ft./hr., the next one 500, and the next 1000. There is every indication that the unit size will go up a good deal more.

The pots used in a plant of this kind are regarded more as oxygen-excluding envelopes than as pots in the generally accepted sense of the term. They are made as light as possible so as to cut down the extraneous weight of metal to be heated up as far as practicable, and thereby increase the overall thermal efficiency of the plant. This, as you can imagine, and as has been suggested by Mr. Oliver, has demanded a good deal of work on heat-resisting alloys, because obviously that object could not be attained without having some effective means of supporting the weight of the charge independently of the pot.

I do not think that I ought to encroach on the authors' opportunity of replying to the points made by Mr. Oliver, but there are just two comments which I should like to make. First of all, suspension bars carrying reasonable weight under operating conditions have been working for a number of years at as high a temperature as 950° C. I give that as a commentary on what has already been said.

I do not think that the authors have made quite clear what they mean by welded construction. They compare a cast Cronite bar with a welded construction. I know what they mean, but I do not think that their meaning is made perfectly clear in the paper. I believe that the welded construction to which they refer is the weld metal of an arc weld built up between the open ends of a split bar, whereas the welding referred to by Mr. Oliver is flash butt welding, which is entirely different.

In passing, and still on this subject of bars, it may be of some interest to mention that bars which have been running under ordinary shop conditions for ten, twelve, and even fourteen years, are still in operation, and are just as pleased with themselves as when they were put in.

There is another comment which I might make

on that, since it is an important factor in the subsequent development of any such process. Flash-welded bars of a different ferrous alloy are being used to-day to carry charge weights as high as 11½ tons at temperatures comparable to those discussed in the paper.

Coming to recuperation, there can be no question, in my opinion, that recuperation pays on all these ferrous materials. Mr. Oliver deduced the saving from recuperation as 20%. I have always assumed, from my experience, that with a plant of this kind we would get an average economy of 15%. There is nothing very special about the building of the pits; they are built of insulated bricks, with in some cases two hot and two cold pots put together, and in others two hot pots and one cold. With this process, and with the shape of the pots and the other features which are peculiar to it, there is a precise temperature control, a uniform heat distribution, and constant conditions from one charge to another, and this, of course, gives you what you are aiming at in the form of a uniform anneal.

There is one point I should like to make on current consumption. I see that this is given in the paper as 180 to 200 units per ton. There are scores of these plants working on cold-rolled steel strip and, whilst I do not quarrel with that figure for one moment, I can bring to mind some installations on which I have been compelled by works records to accept as low a figure as 165 units per ton.

I think that Table I. of the paper is very interesting, and gives a remarkable proof of what can be obtained under workshop conditions.

Mr. W. E. HOARE (Tin Research Institute): The two previous speakers have discussed the question of recuperation, particularly from the point of view of the valuable heat economies that are obtained. It might be mentioned, however, that in this particular case, even if the recuperation operation belied its name and saved no heat at all, it would still be a most important step in the annealing process. The comparatively slow initial rate of heating started in the recuperator pits and continued in the switch-off period in the furnace, enables residual lubricants on the strip to be vapourized and washed out while the charge is at a relatively low temperature. This, as the authors point out, largely avoids breakdown or cracking of the lubricants, and thus considerably benefits the final finish on the strip.

This leads to the second point I wish to raise. The type and character of rolling lubricants have been shown by various workers to affect surface properties of the strip *via* their behaviour in the annealing process. The authors mention that they have experimented with mineral oils, rape oil, and also with certain soluble oils. Have they done any work in this connection with palm oil

or palm-oil emulsions, which are, of course, widely used as rolling lubricants, particularly in the production of cold-reduced strip for tinplate?

One further point: Have the authors discerned any differences in surface finish arising with differences in coiling tension, that is, in differences of tightness of coils? Very tight coiling might conceivably restrict the escape of vapourized lubricants from the vicinity of the strip surface, since the entering atmosphere would not have such ready access to surfaces which are in very close mechanical contact.

Mr. C. H. WILLIAMS (Messrs. Stein & Atkinson, Ltd.): This is obviously a most interesting paper of a practical type, such as a number of us have been wanting, and it deals with plant as installed and working on an industrial basis. It is therefore of immense value in comparing the results which are given with those obtained by other methods. There are one or two points on which I should like some information. There is the question of "sticking." It is suggested that it is the atmosphere which is responsible for the lack of sticking, but I put it to the authors that distribution of heat, tightness of coiling, and time at temperature all have a considerable bearing. In regard to the atmosphere-gas plant, no mention is made of drying the gas and I presume that all the steels which are annealed with this particular atmosphere are of the low-carbon mild-steel variety and that no attempt is made to charge high-carbon steels.

Dealing with the size of the atmosphere-gas plant, reference was made by another speaker to the steady increase in the size of those gas plants, it being suggested that the 1000-cu. ft./hr. plant referred to was large. Actually this is not the case, as for the annealing of wide strip I have intimate experience of units of 15,000-cu. ft./hr. capacity in this country.

On the question of evenness of temperature, the charts which the authors have been frank in including show that with coils charged at 250° C. and after close on nine hours of heating there is a temperature difference of as much as approximately 100° C. between the inside and the outside of the coils. It is only after the heat has been switched off that their temperatures come within about 30° C. Some metallurgists might consider that for many steels the outside of the coils has been overheated. This is certainly a long time for annealing such a charge. The second chart, where care is taken to avoid any excess of temperature on the outside of the coils, takes no less than 15 hr. to bring all temperatures on to the one line. We are so often told that electrically heated furnaces are famed for evenness of temperature when compared with other methods of heating.

With gas firing of the modern type—not the ancient system which this new plant has replaced—and with re-circulating fans, a furnace of roughly double the size and charged with 6 tons of coils is heated in 6 hr., with a temperature differential hardly measurable on the chart, and with no part of the charge overheated above the annealing temperature. This cycle, as far as temperature is concerned, is comparable with the 15-hr. cycle depicted by the authors and, based on the effective cubic capacity of the containers, works out per 100 cu. ft. at an output of 0.85 tons/hr. for gas heating and 0.15 tons/hr. for electric heating.

The use of electricity therefore does not seem to show much advantage in the important respects where advantage is usually claimed.

The authors refer to the saving from recuperation but even so the electric costs are high. Taking the lower figure of 180 units and assuming a rate of $\frac{1}{2}$ d. per unit, which is a low figure, the cost of heat for annealing is 7s. 6d., which is quite a high figure for fuel only. With gas, and depending on the size of the plant, it is possible to anneal with between 2200 and 2700 cu. ft./ton. For the smaller types of furnaces, as described, the higher of these two figures will apply. The cost of gas varies in different localities, but in important industrial districts is between 1s. 6d. and 2s. per thousand cubic feet.

There would thus appear to be advantages for gas heating in cost of fuel, evenness of temperature, and output, for a given size of plant. A higher degree of control over heating rate and greater flexibility of automatic temperature control is possible with gas heating than with electric heating and it entails no more labour.

Mr. G. A. FINCH (Lancashire and Corby Steel Manufacturing Company, Ltd., Corby): I should like to congratulate the authors on this paper, which is a combination of research and works experience on a large scale and a very useful addition to the literature on the subject. There are two points which seem to me to call for comment. The first deals with the controlled atmosphere, and has already been referred to in the discussion. We know that the gas is cooled by a surface cooler, so that the gas entering the furnace is saturated at the temperature to which it is cooled down. What is the maximum dew point which can be allowed in this gas before it effects blueing? In experience with gas annealing it has been found that if the dew point rises above 10° C. serious blueing takes place, and consequently gas driers have to be installed.

My other point deals with the physical tests after the strips have been annealed. It is noted from the Tables in the Appendix to the paper that the maximum ductility and minimum hardness as given by Erichsen and V.P.N. in all cases are

produced by annealing at a very high temperature. In the case of steel *EV* it is 900° C., with *EV2* it is 900° C., with *RT* it is between 750° and 850° C., and with steel *W* it is 800° C. I should like the opinion of the authors on the effects of this mixed structure which is obtained by annealing between the critical temperatures, particularly with regard to deep-drawing properties, tool wear, and directionality in the finished strip.

Mr. R. S. BROWN (Messrs. Rylands Brothers, Ltd.): The authors and their Companies are to be congratulated on publishing a paper of this nature, covering the results of their research and development in the practical sphere. The paper, which is well written, not only emphasizes some excellent features of the annealing process adopted, but also draws attention to a feature which, under some conditions, might lead to trouble.

I refer to the question of temperature gradients shown in Fig. 14. The curve representing the middle-coil outside temperature shows a maximum of 760° C. after which it is cooled to the optimum temperature of 700° C.; during this time the inside of the coil is shown to be still rising in temperature. Conditions of this nature are certain to occur in systems of the type shown in the paper, and the alternative conventional system which incorporates a circulating fan largely overcomes this effect, particularly if the rate of circulation of the atmosphere round the charge is maintained at a high value.

The trouble with charges of the nature discussed in the paper is the dead spot in the centre of the stack. Attempts have been made in the past to deal with this by constructing annealing pots with tubular centres, by means of which heat can be applied in that position as well as from the outside. An arrangement of this kind is difficult to apply to modern plant, but a circulated atmosphere offers an entirely satisfactory solution to the problem.

I suggest, therefore, that the weakness of this particular process is the absence of a fan which, as well as achieving more uniform temperature conditions within the charge, greatly increases the heating rate of the charge as a whole. This has already been referred to by the previous speaker, and my own experience, using an alternative system, would suggest that the heating times shown are excessive. It should be noted that the heating cycle commences at 250° C. and not from cold.

This is my chief point of criticism and I think that the paper has gained in value by a frank publication of the facts, as it is only by this means

that progress in this important field can be measured.

The question of lack of uniformity might not be so very important on dead-low-carbon mild steels, although I know of several instances of grain growth in the outside waps of coiled strip playing havoc with final processing, but if a process of this nature is called on to handle the medium- and high-carbon steels where spheroidizing is required, I believe that it would be incapable of handling this kind of charge under the conditions shown in Fig. 14.

Finally, I should like to ask how the authors manage to hit the exact temperature they want within the charge by shutting off the furnace at an early stage and letting it cool down. During this time, part of the charge is cooling and the rest is heating up, so that uniform conditions are arrived at on the cooling part of the cycle. How do they arrive at the precise mean temperature under these conditions?

Mr. R. WHITFIELD (Incandescent Heat Co., Ltd., Smethwick, Birmingham): There is one small point which I should like to raise. The authors deal with the water, which is the damaging agent in any "neutral" atmosphere, by means of a plain surface condenser. That is all right if it suits a particular mass output, but if the output is to be varied, and high-carbon steels dealt with, then greater care will have to be taken of the moisture content. It is my experience that to cover the range of steels met with nowadays it is almost imperative to add silica gel or some other drying agent, so as to have a controllable dew point down to -40° C. or -40° F. By doing that we can cope with the composition variations which occur.

With regard to welding, we have found that the best results are obtained with atomic hydrogen. I have had a cast tube welded into sections subjected to temperatures up to 1150° C. for three weeks at 24 hr. per day, and it is quite satisfactory. Atomic hydrogen may be more expensive, but it certainly gives the best results at the weld for materials of the high nickel-chromium type.

The PRESIDENT (Dr. C. H. Desch, F.R.S.): I am familiar with this plant, and, comparing the condition in which the coils come out of these pots with some that I have seen from other types of furnace, it is remarkable to see how clean the coils are right up to the edge. The blue edge which gives so much trouble is wholly avoided. I am glad that there has been a discussion on the design and construction.

AUTHORS' REPLY.

The AUTHORS, in reply, said: We are grateful to those who have contributed to the discussion, but, in view of the limited time available, we cannot attempt to deal with all the points raised. The saving of heat by the method of recuperation, mentioned by Mr. Oliver, has been partly covered by Mr. Cutts, and we can confirm that there is a saving of approximately 20% in electrical energy. No special type of insulating bricks is used in the recuperators.

Reference has been made by Mr. Oliver and by Mr. Cutts to the suspension bars which support the charge, and to the good results stated to be obtained with the cast Cronite bars, as compared with the forged nickel-chromium heat-resisting steels. In this respect, the authors feel that an admission is necessary, as, during the late war, it was essential to increase production appreciably and this was done by increasing the temperature of the furnace above the normal one of 750–780°C. The effect of this, however, was to approach the creep strength of the nickel-chromium steels in use as suspension bars, and, occasionally, an appreciable increase in length of these bars was found to occur, whereas the Cronite bars were unaffected under a similar load at this higher temperature. The composition of the Cronite bars was 60/15/20 nickel-chromium-iron with approximately 0.7% of carbon.

There has been some comment on the effect of heating the steel to a temperature above the critical point, and to the effect of the spheroidizing of the carbide on the deep-drawing qualities. Owing to the temperature gradient described, the carbide in the outer rings of the coils must go into solution and is re-formed as pearlite; in other words, this carbide is not spheroidized, but, on the other hand, the carbon content of the deep-drawing steels is so low that this has not been found to be detrimental for most purposes. We would imagine that, for a very deep draw, complete spheroidization may be important.

Mr. Finch has asked how much water vapour can be tolerated in the controlled atmosphere. With the particular atmosphere given in the paper, and the temperature with which we are concerned, the equilibrium concentration of water vapour with respect to hydrogen in the gas is of the order of 7% and therefore we could tolerate up to this amount of water vapour with a high hydrogen content without getting oxidation of the strip under the conditions of working. The whole point is that, in this particular type of plant and with the controlled atmosphere used, oxidation could occur if a flow of gas were maintained throughout the cooling cycle, but this effect is avoided by cooling under a pressure of gas, thus retaining a bright anneal. In the continuous type

of furnace, a similar atmosphere can be used with the same water-vapour concentration to obtain bright annealing, because the rate of cooling of the strip is too rapid for oxidation. These factors must be taken into account when considering the optimum composition of atmosphere for a particular purpose. In reply to Mr. Whitfield, we would heartily agree that, for the annealing of medium and high-carbon steels, not only would dehydration be necessary, but the CO₂ content of the gas would have to be reduced. In such a case, we would not recommend the particular type of atmosphere described in the paper, but a modification of it.

A good deal has been said about gas heating as compared with electric heating, and the use of fans. We think that it is accepted nowadays that, for ease of control and uniformity of heating, the electric furnace is in a class of its own. Mr. Williams considers that a cost of 7s. 6d. per ton for heating is excessive. Gas heating may be cheaper than that, but we claim that the electric furnace has definite advantages in giving ease of control and working, with less trouble than with gas, and we consider that the cost of heating is offset by a low labour cost and an exceptionally low maintenance cost. We do not think that there is any plant with a similar output heated by other means, that operates with such a low cost of labour.

In presenting the paper, however, we have deliberately avoided drawing a comparison between electric heating and alternative methods; it is somewhat dangerous to do so, as there are so many factors to be considered. It is not possible to make a strict comparison between the various methods of heating unless one is dealing with precisely the same product and the same personnel handling the plant in the same works. It is all very well to state that with gas heating a charge of this type could be heated in, say, 5 hr., whereas an electric furnace takes, say, 10 hr. We could rightly say that, if we had a sufficiently large high-frequency generator we could heat the charge in 1 hr., but we have to consider many factors in dealing with these points, and it is necessary to be very careful about making comparisons of this nature.

Fans can be used when necessary, but it should be pointed out that the Whitehead plant is not concerned so much with extreme uniformity of temperature throughout the coil during the heating period, as the product being heat-treated will tolerate a reasonable temperature distribution within the charge, and the plant that has been installed to produce that product is considered to be the most economical for this purpose. Generally speaking, fans are best adapted for

types of work which will permit of the ready circulation of the atmosphere over as great an area of the charge as possible, and we would not say that a charge of coils of strip in such a compact container is an ideal charge in that respect.

The AUTHORS, in a further reply, wrote: We would like to thank Mr. Oliver for his appreciative comments on the paper. We do not wish to make an invidious comparison between forged and cast heat-resisting materials in general. We have no actual figures for the creep strength of the austenitic steels and cast nickel-chromium-iron alloys at various temperatures, and have pointed out only the practical fact that the cast bars were found to have a greater creep resistance when the plant was worked under more arduous conditions than in normal practice. In the old annealing plant, some welding troubles were experienced with the forged nickel-chromium steel bars, when the split ends were filled in with arc-deposited metal. This introduced difficulties in ensuring soundness in the weld, and the properties of the steel in the vicinity of the weld were affected. Flash butt-welding of wrought bars has been an improvement, as stated, whilst Mr. Whitfield has also referred to the advantages of atomic hydrogen welding of materials of the high nickel-chromium type. More recently, wrought bars of newly developed heat-resisting steels have been flash butt-welded, and these steels have proved to be satisfactory for use as supporting bars under high loads at elevated temperatures. It should be mentioned, when the vagaries of castings are referred to, that the cast bars of Cronite are radiographed for porosity before being put into service. A typical composition of the Cronite bar was carbon 0.7%, silicon 2%, manganese 1%, nickel 52%, chromium 16%, tungsten 1%, and iron 25%.

The composition of the base casting, on which the coils of steel strip are loaded, is that of N-Resist cast iron.

With reference to the deep-drawing and cold-pressing steels referred to in Table I. of the paper, these were free from aluminium. The rolling texture of these steels is eliminated by annealing.

We were particularly pleased to have the contribution to the discussion from Mr. Cutts, for the reason that he had been intimately connected with the plant from the early stages.

Mr. Hoare has confirmed our views regarding the beneficial effect of the slow rate of heating of the cold-reduced coils in the initial stages of annealing, apart from economic considerations. With reference to rolling oils, palm oil has not been used to any extent for the cold reduction of strip in the rolling mills under discussion. It is necessary to remove this oil before annealing, usually by the electrolytic cleaning of the coils.

Tightness of coiling is, of course, an important factor in annealing, and, generally speaking, oil staining is more likely to be met on thin-gauge strip, which obviously presents a more solid coil wall than does heavy-gauge material. It would be found that, not only is the elimination of the oil lubricant more difficult in a tight coil, but there would also be a danger from "sticking" of the coil turns. The coils, after cold reduction, are passed through the slitting machines, where they are re-coiled more loosely before annealing. This will partly answer the point raised by Mr. Williams, and it is our opinion that, whereas there are several factors that would contribute to the nuisance of "sticking," the danger from this source is very much less when using annealing gas. This has been confirmed on the older plant when working under exactly similar conditions as regards weight of charge and annealing cycle, but without the atmosphere. Mr. Williams has commented on the size of the gas-atmosphere units referred to by Mr. Cutts. For the annealing of coils of narrow strip, which is dealt with in the paper, gas burners with an output of more than 1000 cu.ft./hr. are considered to be large for electric furnaces in which efficient gas-sealing arrangements reduce the quantity of annealing gas to a relatively small volume. Regarding the 15,000-cu.ft./hr. gas generator, one is tempted to ask why this large quantity of controlled atmosphere is required in a modern furnace installation. The remarks on temperature uniformity have already been partly answered. Mr. Williams is attempting to draw a comparison between the electrically heated furnace under discussion and another type of gas-heated furnace, in which a fan is incorporated. We are not unaware of the effect of heat transfer to the charge by convection, and the more rapid rate of heating and evenness of temperature referred to are apparently obtained by means of the fan-induced atmosphere circulation, rather than by the actual means of heating the furnace. A similar advantage could be claimed if the furnace were electrically heated. With regard to temperature control, a more precise and uniform temperature is assured in a vertical direction in an electric furnace than by other means, and there is only one thing to control, *viz.*, the electric supply to the furnace. With gas-fired furnaces, there are at least two things to control, neither of which is as constant as electricity, nor as simple to deal with. Mr. Williams has referred to the cost of annealing, but it is the overall cost, including maintenance and labour, that must be considered, and not only the cost of fuel for heating the charge. It is from this standpoint that the relative merits of the respective heating methods must be assessed. Finally, it is significant that a large proportion of the narrow steel strip produced in this country is bright-

annealed in electrically heated vertical cylindrical furnaces, similar to those described in the paper.

With reference to the ductility and hardness of the steels, mentioned by Mr. Finch, the effect of heating to temperatures higher than sub-critical, after heavy cold-reduction, is to induce a progressive grain growth. It is considered that the annealing of deep-drawing steels at approximately 700° C., after a suitable degree of cold-reduction to impart the desired grain-size for the application, is better than annealing the steels at higher temperatures. The comments of Mr. Brown are much appreciated. Excessive grain

growth in the outside rings of coiled strip is caused usually by the furnace temperature being too high, resulting in a rate of heating which is too rapid. With regard to the temperature of the charge during the last hour of the annealing period, actually this presents no practical difficulty, the furnace current being switched off when the central thermocouple indicates the required temperature on the recorder. The soaking of the heat through the coil retains the thermocouple at a constant temperature during this period, which is indicated as a straight line on the chart.

THE MELTING SHOP OF THE TURKISH STATE IRON AND STEEL WORKS, KARABÜK.*

By L. COOK (SCUNTHORPE, Lincs.).

SYNOPSIS.

An account is given of the open-hearth plant and practice at the Karabük Iron and Steel Works, which commenced steelmaking operations in 1940. The plant is situated near the Zonguldak coal area, in Asia Minor, and was established by the late Kemal Atatürk as part of the scheme for the industrialization of modern Turkey. Turkish ores of low phosphorus and sulphur content, and other raw materials obtained within the country, are used in the plant for the production of the iron.

The melting shop contains four fixed furnaces of modern design, each of 65 tons' capacity. The furnaces are fired with coke-oven and blast-furnace gas, which is pre-mixed at a central station and conveyed to the shop through a common main. The charges consist of scrap, and hot metal received direct from the blast-furnace. Ore additions are made in the runner and ladle to hot iron that is judged to have a silicon content higher than the desired limit. Details of the furnaces and the materials used are given, together with descriptions of the steelmaking and casting practice for the production of ingots designed for rolling in the mill, without a preliminary reduction in a cogging mill. Summaries of performance figures are included, with a mention of difficulties arising from war-time conditions of supply. Brief accounts of controls, and a description of the methods used for training personnel, conclude the paper.

THE Karabük plant was established by the late Kemal Atatürk as part of the scheme for the industrialization of Turkey. It is situated about 60 miles south of the Black Sea, in Asia Minor, at the confluence of two small rivers, and is served by the railway running between Ankara and the coal-mining area of Zonguldak.

The plant was originally designed to utilize imported phosphoric ores, but during the construction period Turkish hematite ores rich in iron and with a low content of phosphorus and sulphur were discovered at Divrik, in the north-eastern part of Asia Minor, and these ores have been used almost exclusively.

Coal supplies are received from the near-by Zonguldak area, whilst limestone, raw dolomite, manganese ore, and other raw material come from within the country, at no great distances away.

The works were designed by Messrs. H. A. Brassert & Co., Ltd., and a British staff, together with Turkish engineers—many of whom had received a preliminary training in iron and steel works in the United Kingdom—were responsible for the initial operation of the plant. The first cast of steel was made on January 6, 1940.

Layout.

Figs. 1 and 2 show the layout of the melting department. The main building, 496 ft. long, houses four 65-ton open-hearth fixed furnaces,

constructed by The Wellman Smith Owen Engineering Corporation, Ltd. These furnaces, which are fired with mixed coke-oven and blast-furnace gas, are designed to utilize a high proportion of hot iron in the charge.

The hot metal, received direct from the blast-furnaces, is charged from the pit side by means of the two 100-ton Arrol casting cranes, each of which is fitted with a 25-ton auxiliary hoist. Surplus hot metal is machine-cast at the pig-casting machine.

The scrap and oxides are charged into the furnaces by a 5-ton revolving overhead Arrol charger, the charging boxes being carried in reserve on stands situated on the stage level, at the stock-yard side of the working platform.

At the rear of the furnaces, the covered stock-yard is served by a 10-ton crane equipped with a magnet. The filled, weighed boxes of scrap are lifted in clips of three by this crane and are placed on the stands at the stage level, for further handling by the charger. Other materials are similarly transported. The furnace flue gases are led off through flues beneath the level of the stockyard to the 150-ft. high chimneys, situated at the rear of the building.

In the pit the steel is cast into ingot moulds set upon car bogies, the teeming being controlled from a raised platform; the filled moulds are removed on the cars by locomotive to a separate building for stripping. The stripper shed, adjacent to the reheating furnaces and the rolling mill, is supplied

* Received May 3, 1946.

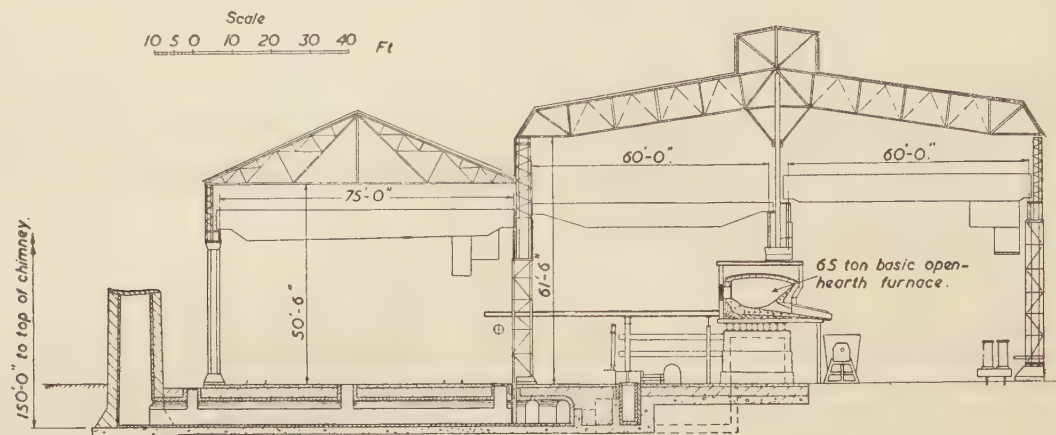


FIG. 1.—Cross-Section of the Melting Department and the Stockyard.

with a combination stripping and ingot-handling crane fitted with an auxiliary hoist.

The slag ladles which are filled from the overflow from the casting ladles are removed by the pit cranes and placed upon waiting carriages for conveyance by locomotive to the outside tipping bank, where the slag is stocked for consumption in the blast-furnace charges. The flush slag, run off over the furnace sills, is collected in cast-steel slag boxes placed on the working platform.

Dolomite stone is calcined in a modern kiln close to the south side of the stockyard, and supplies

of screened and crushed freshly burnt dolomite of good quality are delivered to the requirements of the furnaces. Limestone is burnt in other kilns near the dolomite kiln.

Fuel.

The cleaned mixed gas is supplied through a main from the central gas-mixing station at a uniform pressure of 130 mm. (5.1 in.) W.G., and the respective volumes of coke-oven and blast-furnace gases are automatically controlled by an Askania regulator so as to maintain a mixture of

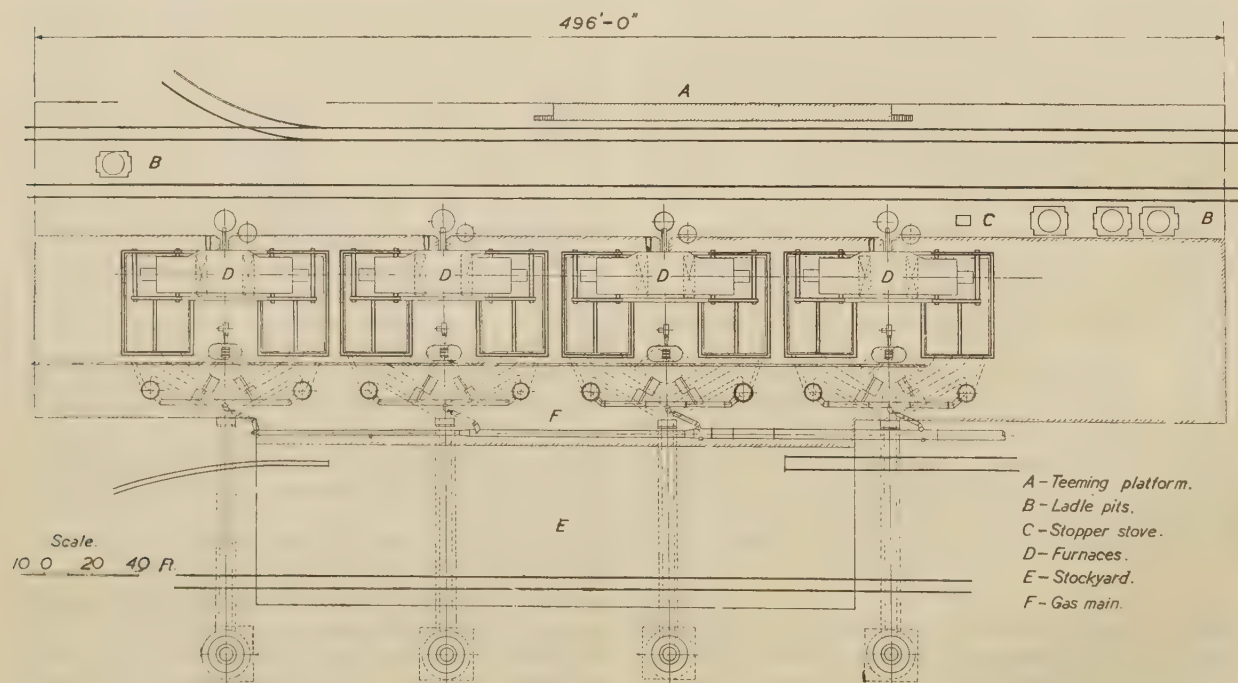


FIG. 2.—Layout of the Open-Hearth Plant.

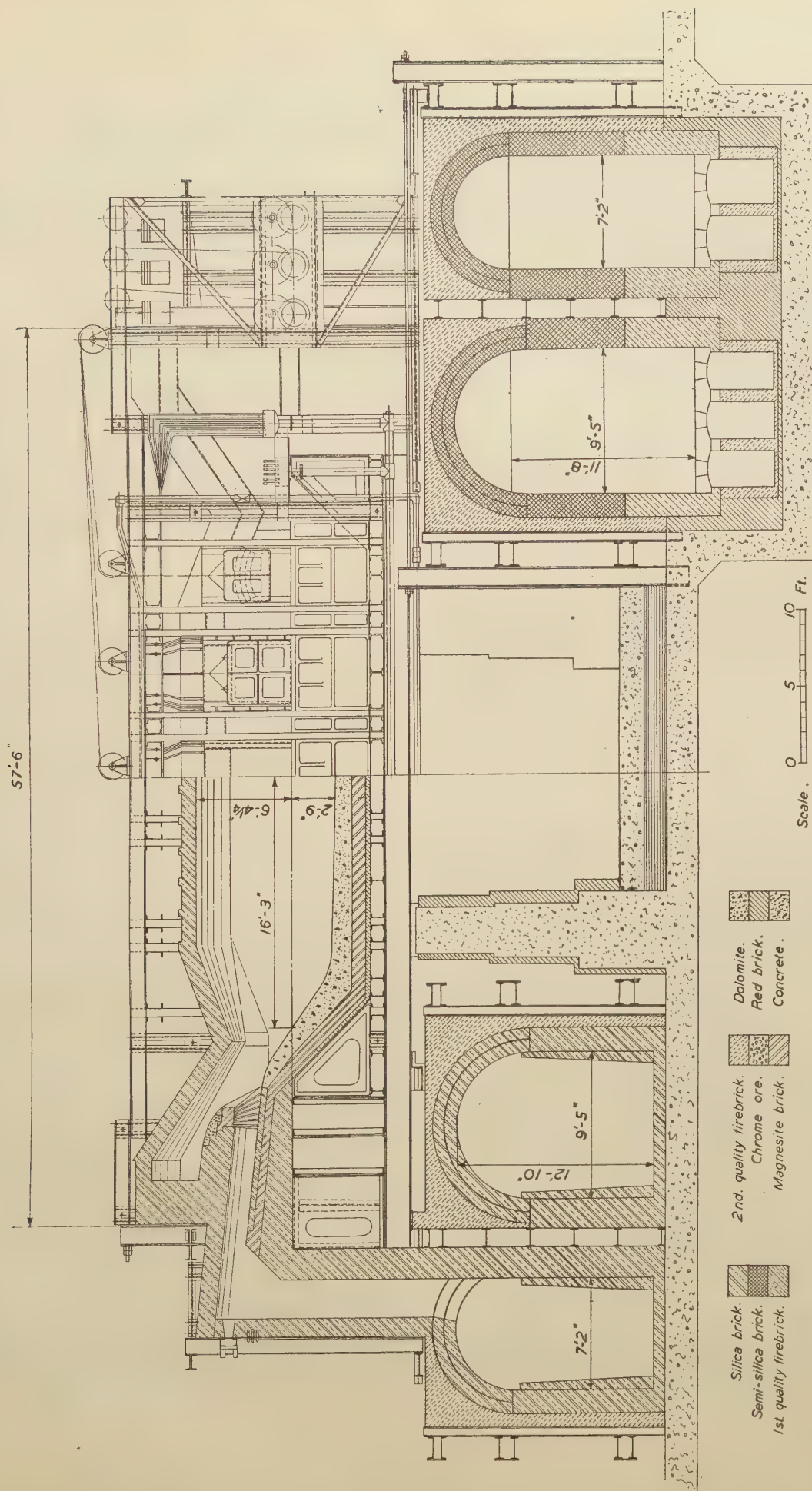


FIG. 3.—65-Ton Furnace.

the required proportions necessary for a gas of the standard calorific value. Every two hours, estimations of the calorific values are made with a Junkers gas calorimeter, and these values serve as a check on the control. Gas-holders of the waterless-seal type are in use on the plant. Typical gas analyses are shown in Table I.

TABLE I.—*Gas Composition (by Volume at N.T.P.).*

	Coke-Oven Gas.	Blast-Furnace Gas.	Mixed Gas.
Hydrogen, % . . .	62.0	...	24.9
Methane, % . . .	19.3	...	7.3
Carbon monoxide, % . . .	5.4	27.4	19.0
Illuminants, % . . .	3.1	...	1.2
Oxygen, % . . .	0.2	0.1	0.1
Carbon dioxide, % . . .	3.5	12.3	9.0
Net kg. cal./cu.m. . .	3770	888	1985
Net B.Th.U./cu.ft. . .	423	100	223

The coke-oven gas is derived from coal which, although bituminous, is near the lignite borderline and has a somewhat low content of hydrocarbons. The methane content of the coke-oven gas is low.

Mixed gas is employed for firing the furnaces and, tapped from the main through small pipes, is also used for the drying and heating of ladles, stopper assemblies, and tap-hole runners. The enrichment of the mixed gas at the furnaces by means of tar spraying is contemplated.

Raw Materials.

Limestone, well sized to a 10–12-cm. (4–5-in.) ring, is used for charging, and burnt lime is reserved for feeding purposes. Manganese ores serve to reduce the consumption of imported ferromanganese. Typical analyses of raw materials are shown in Table II.

TABLE II.—*Analyses of Raw Materials.*

	Raw Dolomite.	Limestone.	Manganese Ore.	Iron Ore.
SiO ₂ , % . . .	1.14	2.10	8.70	5.00
Al ₂ O ₃ , % . . .	1.01	1.00
Fe ₂ O ₃ , % . . .	0.79	0.80
Fe, %	63.00
CaO, % . . .	32.20	53.28	8.68	1.68
MgO, % . . .	18.80	0.44
Mn, %	43.97	...
S, % . . .	0.10	0.10	0.18	0.10
P, %	0.078	0.040

The average analysis of the molten iron as tapped at the blast-furnace for melting-shop use is as follows :

Si, %.	Mn, %.	S, %.	P, %.
1.00	0.70	0.025	0.070

Additions of regulated quantities of fine ore, made in the runner and the ladle at the blast-

furnace, reduce the silicon content of the iron before its delivery to the steel furnace.

Details of the Furnaces.

All four furnaces are of identical construction, dimensions, and design. Drawings of the present construction are shown in Figs. 3 and 4. The

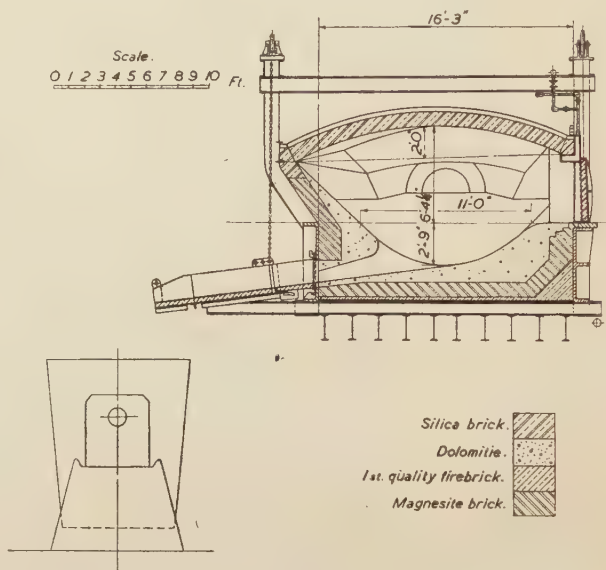


FIG. 4.—Cross-Section at Tapping-Spout.

furnaces show some modifications from the original design, chiefly in port dimensions, height of roof and ramps, lining details, and the introduction of further water-cooling at the gas-port back-wall panels.

Ports.

The cross-sectional area of the gas-port orifice is approximately 3.5 sq. ft., and that of the air port approximately 21.5 sq. ft.

The gas ports are sloped at an inclination of 1 in./1 ft., and the air ports are inclined 8½ in./1 ft. The nose of the gas port, which is covered with chrome paste, is constructed of magnesite bricks and is water-cooled by means of six rings of pipes. Three rows of pipes cool the silica-brick gas-port back wall.

Uptakes.—The cross-sectional areas of the uptakes, at stage level, are : Gas uptakes, 7.5 sq. ft. ; air uptakes, 31.7 sq. ft.

Checkers.—The height from the supporting tile to the upper surface of the top layer of checkers is 10 ft. 11 in. to 11 ft. 8 in., stepped ; the length is 20 ft. 9½ in., the width of air checkers 9 ft. 5 in., and the width of the gas checkers 7 ft. 2 in. Other details are : Number of courses, 22 of semi-silica Peterson-type bricks and 18 of first-quality Peterson-type firebricks ; setting, 9-in. centres, not checked. The air checkers have

auxiliary flues, ten in number, each 1 ft. 3½ in. square.

The height from bottom of flue beneath checkers to crown of checker arch is 23 ft. 9 in., and the height of the flues beneath the checkers, from the floor to the crown of the supporting arch, is 4 ft. 2 in. (minimum) to 5 ft. 2 in. (maximum).

Linings.

The front linings are constructed of normal magnesite bricks carried to within four courses of the skewback, the remaining courses being of normal silica bricks. The three main door openings are well splayed and are provided with water-cooled lintels and jambs, the smaller end door openings having the usual brick arches.

The upper sloping back wall is similarly constructed of magnesite and silica bricks, and is kept well coated with chrome-iron-ore paste during operation.

Roofs and Ramps.

The main roof is supported on special-shaped skewback bricks carried on suspended channels. Under conditions of normal supply of refractories, the roof is constructed of 12-in. silica bricks ribbed every four courses with 15-in. silica bricks, the main roof crown being 6 ft. 4½ in. above the foreplate level and having a rise of 2 ft. The sloped ends of the roof and the ramps are built of shaped 15-in. silica bricks, permitting easy construction.

Hearth.

Dimensions at foreplate level are: Length, 32 ft. 6 in.; breadth, 11 ft.; depth at centre opposite the tap-hole, 2 ft. 9 in.; useful hearth area, approximately 318 sq. ft.

The hearth is made up in the customary manner, a single course of firebricks being laid on the pan plates. The firebricks are covered with four courses of magnesite bricks set in dry magnesite powder, due allowance being made for expansion. The working bottom is put in by ramming the first 6 in. with dolomite and dehydrated tar mixture, the remaining 6 in. being built up layer by layer after the furnace has been heated-up, each layer being sintered-in at a good heat. Basic slag is used as a bond and for the consolidation of the hearth. These hearths have good lives, and it is customary to replace only a portion of the banks adjacent to the lining and to repair the tap-hole at a rebuild.

Slag Pockets.

These are of ample size, and accumulations do not affect working during a campaign. False walls permit the removal of deposits without damage to the main structure of the pockets.

Reversing Valves.

The air and gas valves are of the mushroom type, the latter being water-sealed. The diameters of the valves are 3 ft. 6 in. and 2 ft. 6 in., respectively.

The flue valves are straight-lined and water-cooled, and are carried in water-cooled seats angled to the flues. The reversal gear is electrically operated, but the height to which the flue valves are raised is capable of manual adjustment. A tell-tale on the working platform at each furnace indicates the position of each valve.

Air Fan.

The air required for combustion is supplied by a fan capable of furnishing up to 16,000 cu.m. (20,920 cu.yd.)/hr. The fan is driven by a constant-speed motor, the volume of air delivered being controlled by a valve.

Control Instruments.

Each furnace is equipped with instrument panels carrying the following:

- Air- and gas-flow indicators and recorders.
- Draught indicators.
- Air- and gas-checker temperature indicators and recorders.
- Waste-gas flue temperature indicator and recorder.

The Fery radiation pyrometers for the air checkers are sighted in silica tubes placed above the level of the top course of checkers in the wall at the opposite end to the slag pockets. The base-metal thermocouples for the gas checkers are placed in shielding tubes inserted half-way up the checker height in the wall, likewise at the end opposite to the slag chambers.

A central indicator on the working platform shows the gas pressure in the main.

Refractories.

Many difficulties have been experienced in rebuilding the furnaces in war-time. In most cases it has been quite impossible to secure supplies of the bricks originally specified for the construction, and repairs have been executed from stocks of bricks, many of which had been designed for other purposes and required cutting to the desired shape. These have been supplemented with salvaged bricks and, often, others of inferior composition, obtained from any available source. Frequently, roofs have been constructed from normal 9-in. silica bricks. As a natural result of these refractory difficulties, furnace campaigns have been shortened, the average being 178 charges, as against 330 charges obtained with a construction using bricks of normal composition and dimensions, and repair times have been lengthened. Under these circumstances, it is

impracticable to give details of normal refractory consumption.

Furnace Performance.

The Karabük plant, from the start, has been severely hampered by the war-time difficulties of supply of essential materials, and production has been possible only to the limit of supplies, instead of to the maximum capacity. Nevertheless, encouraging results have been obtained, the record week's furnace production being 1280 metric tons, from the *C* furnace, the 18 charges tapped out including rail steels and up-run slab ingots for plates, the remainder being of semi-killed steel required for light sections and made to the following specifications :

C, %.	Mn, %.	P, %.	S, %.
0.10-0.15	0.35-0.45	0.040, max.	0.040, max.,

the fuel consumption, calculated over a monthly period, being 1.1×10^6 kg. cal./ton of steel. Ingot production has often been at the rate of 10 metric tons/hr.

Typical furnace performance is given in the following summaries of two consecutive weeks :

C Furnace.

Week Ending :	4/11/44. Metric tons.	11/11/44. Metric tons.
Charge :		
Scrap	427.38	390.39
Cold iron	141.86	241.06
Hot iron	594.30	482.73
Iron ore and scale	156.40	155.60
Limestone	60.40	53.90
Ingot tonnage	1194.44	1140.23
Working hours	157.75	148.9

Heating-Up Preparatory to Gassing.

Flares put through the three main doors and supplied with mixed gas, are lit up, and the temperature raised at a steady rate of 10°C./hr. A small coke fire is suspended at the end of each flare pipe as a precautionary measure.

Further flares, each with a small coke fire, are arranged in the slag-chamber wickets of the air and gas checkers at the end of the furnace where it is intended eventually to introduce the main gas at the gassing, and the flue dampers are so arranged that the greater proportion of waste heat also passes down that end of the furnace, special attention being paid to warming the gas checkers.

A fire is lit up at the stack bottom, and the stack damper height is controlled to assist the regulation of the furnace temperature, which is indicated by means of thermocouples.

Gassing.

A thorough examination of all possible sources of air infiltration at the valves, flues, checker walls,

and uptakes, is made before gassing proper is commenced, and suitable remedies are applied to any deficiencies.

Telephonic communication is made to the gas-control department, and the furnace is gassed in the customary manner with mixed gas, after the usual purging precautions have been taken.

The furnace is allowed to heat up steadily with a gas flow of 2000 cu.m. (2616 cu.yd.)/hr. until the first reversal, which is usually 6 hr. later.

Operating Conditions.

Checker temperatures are carefully controlled by means of the adjustable flue dampers, which regulate the proportion of waste gas passed through the air and gas checkers, the optimum flame conditions being obtained when the pyrometer readings of the air and gas checkers are 1000-1200° C. and 900-1000° C., respectively, the actual temperatures of the preheat being, of course, higher.

Periodic estimations of the calorific value of the mixed gas, made at the gas-control department, are telephoned through, and the results are written on a board at each furnace.

Under normal conditions, 4000 cu. m. (5232 cu. yd.) of mixed gas are required per hour for melting purposes.

Care is exercised in the maintenance of the gas ports to the required size and shape. Twice during each charge the port wickets are opened and the ports inspected, a gauge rod, bent at right-angles to the required size, being inserted, and any departure from the original conditions is speedily rectified.

Frequent waste-gas samples taken daily at each furnace are analysed with an Orsat apparatus, the usual oxygen content being 1-3%. Charts are exhibited giving guidance as to the air/gas ratio required under standard conditions.

The draught to the stack, as indicated from a tube inserted in the stack flue about 14 ft. from the reversing dampers, is regulated during normal working conditions to between 22 and 25 mm. (0.87 in. and 1 in.) W.G., and the waste-gas temperatures, recorded from a thermocouple in the same position, vary between 425° and 500° C.

Operations.

Bottom and Tap-Hole.

Strict attention is paid to the maintenance of good hearth conditions; after each tap the depth of the hearth is measured with a rod bent at right-angles to the standard measurement, the banks are inspected, and any requisite repairs are carried out. Calcined dolomite is used for the usual repairs, but calcined magnesite is employed for the repair of deep pockets, which are drained with the assistance of compressed air.

The tap-holes, kept to the required size, length, and level, are closed with coke breeze, plugged with clay from the tapping side, and lightly fettled from the charging side.

Charging.

Charging is commenced with the allotted proportions of light scrap, followed by scrap of a heavier nature, care being taken to distribute the charge properly to avoid deflection of the flame. When half the required total of scrap has been charged, the calculated quantity of limestone and ore is added, together with an amount of manganese ore to supplement the residual manganese.

The remainder of the scrap is then charged and, after a short delay to enable the dolomite used in fettling to become sintered into position and the scrap to become heated up, the whole of the hot metal required to complete the charge is poured through the chute in the pit side of the furnace. If the hot metal available is insufficient, the charge is completed with cold basic iron of standard analysis. If there is any delay in the arrival of the hot metal from the blast-furnace, cold iron is added at a given rate until the hot metal arrives. The timing of the hot-metal addition is regarded as important, for reasons stressed by Knight,¹ and close contact is maintained with the blast-furnace department.

The usual charges consist of 25 metric tons of scrap and 40 metric tons of iron, a typical charge for a cast of normal low-carbon semi-killed steel being as follows :

	Metric tons.
Scrap	25.3
Hot metal (Si, 0.99%)	40.5
Iron ore (Fe, 63.0%)	7.98 (5½ boxes)
Manganese ore	2.4 (2 boxes)
Limestone	3.04 (4 boxes).

1¼–2½ hr. are occupied in charging and fettling.

Melting.

During the melting-down stage there is always a considerable amount of foaming at the surface of the bath, and it is often necessary to reduce the heat input for a while in order to avoid damage to the furnace brickwork. Evans² gives maximum proportions of iron (Si, 0.3–0.4%; P, 1.2–1.4%; Mn, 1.0–1.2%) that can be conveniently carried in fixed furnaces with varying percentages of methane in the gas, with given conditions, and without the aid of artificially produced luminosity. He states that grey and kishy irons will reduce the proportions, whilst low-silicon irons will increase it. Operations at Karabük dealing with iron of a different type and with gas of a low methane content, have shown that the severity of the foaming is influenced by the proportion of

iron in the charge and the silicon content of that iron. These factors are regulated, as far as is possible, with a view to obtaining the maximum output consistent with the minimum risk of damage to the refractories.

With every charge a regulated quantity of flush slag is run off over the foreplates into cast-steel slag boxes placed on the working platform.

Under normal conditions, the melting period is completed in 3½–4½ hr.

Refining, Finishing, and Tapping.

When the bath has settled down and boiling has commenced, slag and metal samples are drawn, inspected, and sent to the laboratory for analysis. Rapid estimations are made of the carbon and manganese contents of the metal sample, the carbon being determined by the quick volumetric combustion method. Estimations of phosphorus and sulphur on the bath samples are considered unnecessary, as the percentage of these elements is always sufficiently low at the melt. Slag samples are analysed during the refining stages for total iron content.

Heats are charged to have a sufficient margin of carbon at the melt to permit ore or mill-scale additions. The quantity and rate of the additions are determined by the usual considerations of temperature, carbon content, iron percentage of the slag, and the requirements of the particular cast.

The amount of lime added is dependent on the appearance of the slag sample, the total iron content, and the physical condition of the slag. Occasionally, fluorspar additions are substituted for lime additions, to take into solution dolomite which has become detached from the hearth.

Manganese-ore additions are made in the bath when normal semi-killed steels are made, a pan of ore being added when the carbon content approaches 0.25–0.30% of the specified final content. This addition is followed by a gradual increase of manganese in the bath to give a content at the tap of 0.30–0.40%.

Tests for bath temperature are made by the customary rod-and-spoon methods, the Schofield-Grace quick-immersion thermocouple not being available in Turkey at the time of writing.

When the charge is about to be tapped, the final bath samples are despatched to the laboratory and the removal of the stopping from the tap-hole is commenced. On the receipt of the analyses results, the furnace is tapped, the oxygen lance being employed if necessary.

The final slag samples are retained in the laboratory for routine estimations of lime and silica, the results being recorded, together with other cast data, for reference.

A representative finishing slag of a 0.10–0.15%

carbon, normal quality semi-killed steel is as follows:

SiO ₂ , %.	Al ₂ O ₃ , %.	FeO, %.	Fe ₂ O ₃ , %.
19.0	2.6	9.4	1.9
MnO, %.	CaO, %.	MgO, %.	P ₂ O ₅ , %.
16.9	41.9	6.6	1.2

The small quantities of ferromanganese which may be required for adjustment to the specification are added from the tapping side, together with the quantity of ferrosilicon required for the particular cast. With ordinary quality low-carbon steels required for plates, &c., 40 kg. (88 lb.) of 85% ferrosilicon are added in the runner.

Sheet-bar steels are made as the ordinary low-carbon steels, with additions of ferrophosphorus made in the ladle.

Slightly higher carbon steels of the range 0.18–0.25% of carbon are tapped "catching the carbon" and, as the bath approaches the specified carbon content, the rate of carbon fall is checked by the addition of a little spiegeleisen, or cold hematite iron. With ordinary steels of this carbon range and a manganese content of 0.50–0.60%, required for sections, no ferrosilicon additions are made to the ladle.

Rimming steels are made with an increased basicity and a higher total iron content of the finishing slag, and the charges have sufficient carbon at the melt to ensure a good boil throughout the refining stage. Additions of manganese ore in the bath after the melt are omitted, and the aluminium additions in the ladle are governed by a rate based on the total iron content of the slag at the tap. The ferromanganese additions are made in the runner.

For higher-carbon steels, such as rail steels, the furnace is charged with a reduced quantity of ore, and the limestone charge is slightly increased to give a lime/silica ratio of 2.2–2.4. Feeding of the bath is limited to mill-scale additions, and is stopped when the carbon is 0.25–0.30% over the specification. As the carbon boils down steadily to within 0.10% of the required specification, small additions of spiegeleisen are made to the bath to slow up the rate of carbon fall. The remaining few points of carbon are worked out with a rod. Half the total of ferromanganese estimated as necessary to bring the steel to the specified manganese content is added to the bath, the remainder being added with the ferrosilicon in the runner. Consistent final analyses are obtained in the manufacture of rail steel required to fulfil the requirements of the Turkish State railways:

C, %.	Mn, %.	Si, %.
0.43–0.46	1.00–1.15	0.12–0.20

With all types of steel made, pyrometer readings are taken of the steel stream leaving the furnace, using a disappearing-filament pyrometer, and the

charges are tapped at a good heat. Ladles are held in the pit, before lifting the stoppers, for varying lengths of time, depending upon the pyrometer readings, the rate of flow from the furnace, the type of steel made, and the teeming requirements.

Casting Pit.

Ladles, Stoppers, and Nozzles.—Lining details of steel ladles of 70 tons' nominal capacity are:

Safety lining of 1 in. increased to 2 in. in the lower third of the ladle height. The working lining is composed of 6-in. firebricks of Turkish origin. No slurring of the lining is permitted, and the average number of casts per lining before renewal is sixteen.

Twin stoppers are fitted to each ladle, and all stoppers are made up during the day-time by a stopper-maker and his assistant. Stopper heads are of the screw type, and the completed stoppers are dried in a vertical gas oven, precautions being taken to use them in the order of assembly.

All ladle gear is standardized, as is the method of ramming and drying the nozzles and setting the stoppers in position. Jigs are provided for the vertical positioning of nozzles. Entries in a ladle book and on the cast sheet record the identification number of the operator responsible for preparing the ladle.

All nozzles are boiled in dehydrated tar for a minimum of 4 hr. before use, it being found that the home-produced nozzles give improved service after such treatment.

Ingot Moulds and Bottom Plates.—The ingot moulds used for the production of 1.5-metric-ton ingots of normal steel are shown in Fig. 5; the internal dimensions of these moulds are as follows:

Top cross-section, length × breadth, 356 mm. × 356 mm. (14 in. × 14 in.).
Bottom cross-section, length × breadth, 406 mm. × 406 mm. (16 in. × 16 in.).
Height, 1373 mm. (4 ft. 6 in., approximately).

The thickness of the mould walls is 76 mm. (3 in.), and the ratio of mould weight to ingot weight is unity.

The moulds used for killed steel have similar cross-sectional dimensions, but are recessed in the upper 425 mm. (16.7 in.), to take refractory tiles. These moulds, which are used with undished up-run bottom plates, are 1473 mm. (4 ft. 10 in.) high.

The moulds used for slab ingots have the following internal dimensions:

Top cross-section, length × breadth, 406 mm. × 120 to 140 mm. (16 in. × 4.7 to 5.5 in.).
Bottom cross-section, length × breadth, 500 mm. × 145 to 165 mm. (19.7 in. × 5.7 to 6.5 in.).
Height, 1473 mm. (4 ft. 10 in.).

The corners of the mould have a radius of 40 mm. (1.6 in.), and the weight of the slab ingot is 0.88 metric tons.

All ingots are designed for rolling in the mill without a preliminary reduction in a cogging mill.

All down-run moulds are placed on dished bottom plates fitted with replaceable chill-cast iron inserts, which form the base of the pouring basin, the moulds being accurately located by means of lugs on the bottom plates. All moulds and bottom plates are manufactured at the plant.

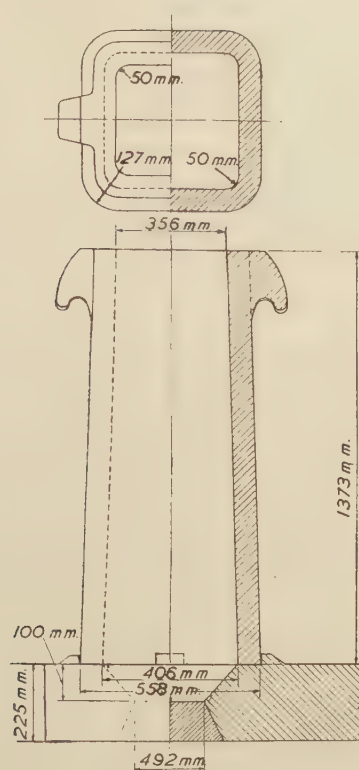


FIG. 5.—Standard 1.5-Metric-Ton Mould and Bottom Plate.

Bottom-Teeming Equipment.—The equipment provides for the pouring of the steel down a fire-brick-lined centre funnel and for the distribution through brick runners. Great attention is paid to cleanliness, and all assemblies are blown out with compressed air before use. Bottom plates are available for the bottom teeming of groups of four or eight 1.5-metric-ton ingot moulds, and for groups of up to fourteen 0.88-metric-ton slab moulds.

Mould Preparation.—For carbon steels the moulds are hand cleaned with wire brushes, and smoked with burning pitch before use.

Method of Teeming.—Bottom-teeming and top-pouring methods are employed for the casting of the 1.5-metric-ton ingots, the method used depending on the standardized practice for the type of steel being made and the purpose for which it is designed.

Slab moulds are invariably bottom teemed, the

bulk of the cast being in groups of 14 moulds, the finishing being in a group of four moulds followed by ordinary 1.5-metric-ton moulds top poured.

Ordinary steels are top poured into 1.5-metric-ton moulds through twin 1-in. nozzles, the average time to fill a mould being 57 sec.

Mould Additions.—Much of the steel made is of the “balanced” or semi-killed type, and the aluminium mould additions are made when the mould has been filled to within 3 in. of the ingot height, the amount and timing of the additions being under the strictest supervision. With up-run slab ingots of this quality, the additions are made down the central runner, again when the steel is within 3 in. of the required height.

Killed steels are covered with coal ash as an insulating medium when the moulds are full.

Stripping.—Moulds are stripped as soon as is practicable to allow for cooling before re-use. All moulds are examined after stripping, and any showing cracks or internal crazing are scrapped.

Mould Records.—Data are filed of mould life and usage, and also the reasons for the ultimate withdrawal from service; the periodic reports are forwarded to the department responsible for mould manufacture.

Ingot Inspection.—All ingots are inspected after stripping and before delivery to the mill, and records are kept of relevant details. Ingots found to be defective are retained for dressing, &c.

Charges.

Hot Metal.

The hot metal supplied from the blast-furnace, whilst of excellent quality, is subject to the usual

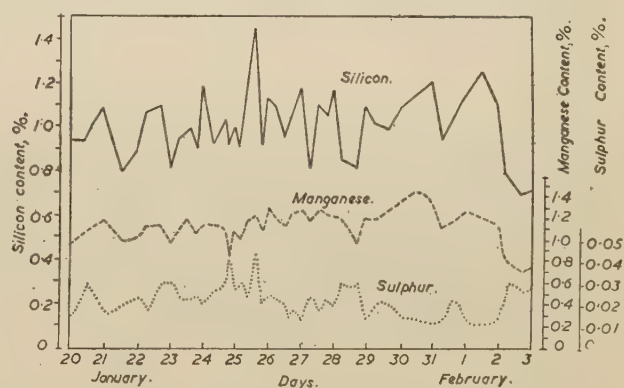


FIG. 6.—Analysis of Hot Metal As-Tapped.

fluctuations in silicon content associated with blast-furnace practice, and the absence of a mixer furnace makes it necessary to employ some method of regulating the composition of the metal charged into the furnaces if irregularity of operation and of quality of product are to be avoided. Fig. 6 illustrates the fluctuations in analysis of the hot metal tapped at a blast-furnace over two repre-

sentative and consecutive weeks. The sulphur content is always sufficiently low to cause no concern.

The desired silicon range is 0.8–1.0% and the method employed to reduce the percentage of silicon in the irons above this range is to add a quantity of fine ore in the runner and ladle at the blast-furnace, the weight of ore added being proportional to the weight of hot metal.

From the analyses of a large number of samples it would seem that, under normal conditions, the reduction of silicon is fairly constant for a given original silicon content and a given addition of ore, but the amount of the reduction is roughly related to the original percentage of silicon, the greater reductions being obtained with the higher original percentages. The average reduction obtained with the usual ore addition of 3% of the hot metal is 0.2%.

In practice the silicon content of the iron is judged from the fracture of a sample of untreated iron taken at an early stage of the tap. The sample is forwarded to the laboratory attached to the blast-furnace for rapid analysis. The sized ore is added in the runner, the amount of ore depending on the estimated weight of hot metal in the ladle. The metal ladle and its contents are weighed and despatched to the melting department, and the silicon estimation and information of ore additions are telephoned through.

A sample of the ore-treated iron is taken as the metal is charged into the furnace, and the analysis is available later for any adjustment.

In occasional cases where the silicon in the untreated iron exceeds 1.20%, a proportionate amount of cold basic iron is charged, and the amount of hot metal utilized is correspondingly reduced.

Scrap.

The amount of scrap charged is kept constant at 25 metric tons per charge, and is not varied except during occasional shortages of supply. The varieties of scrap are proportioned out amongst the furnaces. The quality of the scrap charged is good, and there is little possibility of entangled dirt being charged into the furnaces.

Limestone.

The amount of limestone charged is taken from a scale based on the calculated requirements of charges of varied composition. Due allowance is made for removal of flush slag which is regulated to be constant in quantity with charges of similar composition. The weight of limestone charged provides for the addition of a small quantity of lime at normal melts. The average quantity of lime added per charge is 0.46 metric tons.

Charging-Box Weights.

Periodic checks are made on the weights of various materials held by a standard charging box.

Time Controls.

Charge times have been sub-divided into suitable divisions, *viz.*, fettling, charging, melting, and refining and, as a result of the collection of data over a long period, standard times for each type of charge have been established.

The operators appreciate that under normal conditions the standard times are attainable, and that extension of these times are due to causes which, in most cases, are capable of being described in exact terms such as, for example, mechanical breakdowns, deficiency in gas supply (which can be stated in terms of calorific value or cu. m. per hour), &c.

Maintenance.

Mechanical equipment is inspected every shift by a competent person, and reports are made. On the basis of these reports, arrangements are made for repairs to be carried out at suitable times. Furnace structures and equipment are examined frequently, and schedules of repair work arranged.

Lists of working tools are exhibited at each furnace and also in the pit, and the actual tools are inspected daily.

Future Developments.

Future developments are contemplated to increase the present plant capacity of 150,000 tons of ingots a year.

Present extensions include the erection of a 4-ton direct-arc electric furnace of modern design, together with ancillary equipment.

Training of Personnel.

The Turkish staffs, with the exception of the engineers trained abroad, started without experience of steelmaking, and in many cases without previous industrial experience.

Training in the first instance was by observation of the experienced staff, and as members of that staff departed the positions were filled by Turkish nationals, who were given a course of lectures and practical demonstrations.

Regulations with explanatory notes, covering all branches of melting-shop work, have been issued in the form of a printed book to all responsible operators.

Industrial schools for young persons intended for future apprentices have been established, the lecturers being members of the works staff who are qualified as engineers and metallurgists. The capacity of the trainees to acquire knowledge and skill may be judged from the fact that the melting

department is now entirely staffed and operated by Turkish nationals.

Acknowledgments.

The author wishes to thank the General Directorate of the Sümerbank for permission to publish this paper. His thanks are also due to Bay Sidet Etiker, General Manager of the Karabük Plant, to Bay Ekrem Kaprali, Bay Aziz Aksu, and to others.

Acknowledgments are due to Mr. A. Robinson, of the Appleby-Frodingham Steel Co., Ltd., for suggestions, and to Mr. W. H. Jones, of Messrs. Simon-Carves, Ltd., for information on the Zonguldak coal.

REFERENCES.

1. R. L. KNIGHT: *Journal of The Iron and Steel Institute*, 1943, No. I., p. 233 p.
2. R. W. EVANS: *Journal of The Iron and Steel Institute*, 1944, No. I., p. 395 p.

CORRESPONDENCE.

Mr. E. F. BROWN (Skinningrove Iron Co., Ltd., Saltburn-by-the-Sea) wrote: Mr. Cook states that by the addition of 3% of fine ore the silicon content of the blast-furnace metal is reduced by 0.20%. Will he give the exact size and a complete analysis of the ore used, and also any reduction of other elements in the metal?

The methods adopted for adding the ore and for the removal of the slag formed by the reaction are not discussed in the paper, and it would be appreciated if further details could be given.

Further, will Mr. Cook state the temperature of the metal before and after the addition of the ore?

AUTHOR'S REPLY.

The AUTHOR wrote in reply: The hematite fines used are passed through a $\frac{3}{8}$ -in. screen. An analysis of the ore is as follows:

Fe, %.	SiO ₂ , %.	S, %.	P, %.	Mn, %.	CaO, %.
65.2	3.8	0.10	0.10	0.12	2.70

The ore is dried before use. There is a loss of 0.35–0.40% of manganese in the metal treated. The ore is shovelled on to the metal as it flows

in the runner from the blast-furnace. The frothy slag which is formed chills in transit to the open-hearth, allowing the metal to be poured through an opening which is made at the lip of the transfer ladle. The slag remains on the top surface of the ladle and is cleaned off after pouring.

The author regrets that he has no information of the temperature of the metal before and after the addition of the ore.

GAS-CARBURIZING.*

BY IVOR JENKINS, M.Sc. (COMMUNICATION FROM THE STAFF OF THE RESEARCH LABORATORIES
OF THE GENERAL ELECTRIC CO., LTD., WEMBLEY).

(Figs. 9 to 24 = Plates XXVII. to XXXIV.)

SYNOPSIS.

The mechanism of carburization in solid and in gaseous media is discussed, and it is shown that in pack-carburizing the atmosphere surrounding the work is rich in carbon monoxide and hydrogen. It is considered that the hydrogen plays an active rôle in the basic carburizing reactions, possibly by forming hydrocarbon gases which carburize the steel, or by promoting the removal of surface films of carbon dioxide.

The ideal carburizing atmosphere is one which maintains the maximum rate of carburization throughout the period of treatment, is readily controlled to give the desired carbon content and depth of case, and does not stain the work.

Raw hydrocarbon gases, such as town's gas, propane, &c., give rise to heavy sooting which interferes with the carburization process and leads to poor and non-homogeneous cases. Sooting can be reduced by diluting the hydrocarbon, and results are reported of the carburization of commercial case-hardening steels in propane diluted with air and with burnt town's gas. Whereas heavy cases of hypereutectoid composition can be obtained, the presence of active decarburizing agents in the diluting atmosphere necessitates a high concentration of propane in order to obtain the maximum rate of carburization, and such conditions lead to excessive sooting of the work.

A more suitable diluting medium is one containing no active decarburizing gas, and in this respect controlled atmospheres which are sensibly free from carbon dioxide and water vapour have given very encouraging results. The concentration of hydrocarbon necessary to give the maximum rate of carburization is sufficiently small to reduce sooting to negligible proportions, and control over the surface concentration of carbon in the case is readily achieved.

Controlled atmospheres containing carbon monoxide and hydrogen, with or without nitrogen, and approaching the composition of the atmosphere found in pack-carburizing experiments, have proved to be quite strong carburizing agents; brief details of the generation of such atmospheres and the results obtained in carburizing commercial steels with them are reported.

The condition of the steel surface before carburization may have a marked effect upon the rate of carbon absorption, and it has been found that activation of the surface by "gas-etching" leads to a very pronounced increase in the rate of carburization above that obtained with rolled or machined surfaces.

It is shown that carburization of steel near to its A_3 point can lead to a non-homogeneous case, and the mechanism of carburization below the A_3 point is discussed.

A brief note is added on the relative stabilities of cementite and of solid carbon, following certain observations during the work on gaseous carburizing processes.

I.—INTRODUCTION.

THE carburization of iron and steel may be effected by heating in a solid, liquid, or gaseous carbon-containing medium, which at high temperatures provides a supply of nascent carbon for absorption by the material being carburized. By controlling the temperature and time of treatment, the concentration of carbon in the surface of the steel and the depth of penetration may be varied over wide limits. Up to the present time, the process mainly used in this country has been that of box- or pack-carburizing, in which the steel is heated to the necessary temperature in a solid

carburizing compound, usually a mixture of hard-wood charcoal and an oxide or carbonate of the alkalis or alkaline earths. Carburization of the steel surface to a hypereutectoid concentration of carbon may be obtained after some time at temperature, and with care in the sealing of the box, oxidation and sooting of the work can be restricted to a minimum. With experience, the conditions of time and temperature of treatment to ensure the necessary degree of carburization can be established, but by modern standards of heat-treatment practice the process has certain objectionable features. Among these is the general lack of control over the process, with regard both to the

* Received June 11, 1945.

temperature of the packed work and to the basic reactions taking place in the box. In addition, the economic aspect has to be considered, which involves the storage and handling of large quantities of carburizing compounds and the cost of heating the carburizing compound and the heavy carburizing boxes to the necessary temperature. In many cases the ratio of the weight of the box and its contents to that of the work being treated is as high as 3 or 4 : 1.

Liquid carburizing agents are used industrially to a considerable extent and are of more or less the same composition, namely, a 50 : 50 mixture of sodium cyanide and sodium carbonate. From the point of view of ease of operation, temperature control, and cleanliness, the process is superior to pack-carburizing. Nitriding as well as the carburization of the steel takes place, but the maximum surface carbon content which can be obtained economically does not exceed about 0.8%. On the whole the process is not suitable for the treatment of massive parts or for the production of deep cases.

Carburization in gas is by no means of recent origin, although industrial development of the process in this country has been slow. In 1879 Ramsden¹ patented a process for the cementation of iron either by gas produced from hot charcoal soaked in a solution of potassium carbonate, or by ammonia preheated over hot charcoal. A few years later Krupp² and others³ patented the carburization of armour plate in various hydrocarbon mixtures, whilst the maintenance of a flow of hydrocarbon gases through a carburizing compound was also advocated. Mixtures of ammonia and hydrocarbons were also used, but the first large-scale industrial application of gas-carburizing followed the taking out of a number of patents by Machlet⁴ and led to the introduction in America, in 1910, of a horizontal rotating retort furnace for the carburization of various small machine parts in an atmosphere of pure hydrocarbon, coal gas, or oil, sometimes diluted by bubbling it through a solution of ammonia in water. The publication shortly afterwards of Giolitti's⁵ book on the cementation of iron and steel indicated the possibilities of carburizing in hydrocarbons diluted with inert gases to minimize soot-formation due to decomposition of the carburizing gas. This principle has formed the basis of most of the subsequent development work on processes suitable for industrial application, but it is only in recent years, since the rapid growth of controlled-atmosphere processes, that any real advance has been made. In this respect, probably because of the ready availability of industrial gases high in hydrocarbons, American practice has progressed far beyond that at present obtaining elsewhere, and the A.S.M. Symposium⁶ outlining the processes in

use in that country is a most valuable contribution to this very important subject.

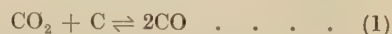
Apart from the work of Giolitti and more recently that of Bramley and his co-workers,⁷ who studied the cementation of iron in pure and carburetted carbon monoxide, there have been very few publications dealing with the carburizing properties of pure and complex gas mixtures which are suitable for use on an industrial scale. The present paper gives the results of an investigation which has been carried out over a period of years at the Research Laboratories of the General Electric Co., Ltd., into the development of industrial carburizing atmospheres.

II.—THE MECHANISM OF CARBURIZATION.

A preliminary consideration of the mechanism whereby carbon is transferred to steel in both the solid and the gaseous carburizing processes is advisable in order that the problem associated with the development of a gas-carburizing process may be more fully appreciated.

Pack-Carburizing.

In solid carburizing, the reactions whereby carbon is transferred to the steel are essentially gaseous. Enos⁸ passed nitrogen through a carburizing compound at temperature, and more or less completely suppressed the carburization, thus confirming that the process is not one of direct transfer of carbon in the solid state. The generally accepted view is that carburization is primarily effected by carbon monoxide, generated by a reaction between the charcoal and the air occluded in the carburizing container. During the early stages of heating, the gas formed is principally carbon dioxide, but at higher temperatures the concentration of the dioxide relative to the monoxide decreases in order to satisfy the equilibrium :



Carburization of the steel then proceeds *via* the breakdown of the carbon monoxide and may be represented by the equation :



The carbon dioxide formed in reaction (2) combines with the charcoal to form more monoxide and thus the cycle of reactions is completed. The main function of the carbonate energizer is to provide a supply of carbon dioxide by slow dissociation at the carburizing temperature, and thereby increase the concentration of carbon monoxide in the box. Oxide energizers function in a similar way, by forming carbonates with the carbon dioxide at low temperatures and later evolving the gas at the carburizing temperature.

Gases in a Carburizing Box.

Much has still to be learned of the pack-carburizing process as a whole, and a complete understanding of the various reactions involved is important in that it may have a bearing on the development of atmospheres suitable for carburizing. One fact which has clearly emerged from the various investigations on the subject is that the process of carburizing by carbon monoxide is speeded up considerably in the presence of solid carbon. Carbon monoxide alone carburizes steel very slowly, although Bramley and his co-

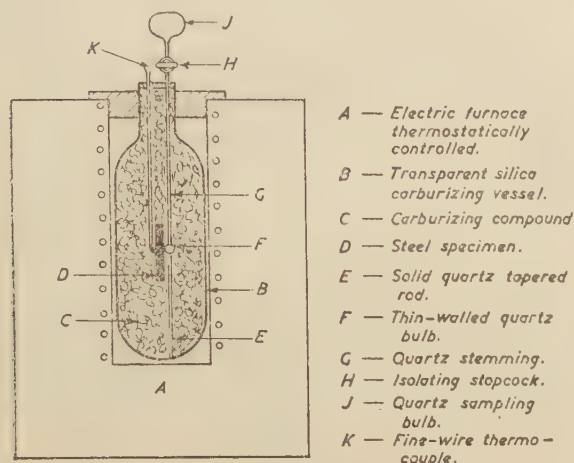


FIG. 1.—Apparatus for the Extraction of a Sample of Gas from a Pack-Carburizing Box.

workers⁷ have shown that at high gas velocities results may be obtained comparable with those in pack-carburizing. However, the effect of gases other than carbon monoxide must be considered in box-carburizing. Water vapour absorbed in the charcoal of the carburizing compound appears to influence considerably the composition of the atmosphere inside the container, as the following experiments have shown.

Samples of 3% nickel case-hardening steel, $5.0 \times 1.25 \times 0.3$ cm. thick, were carburized in fresh mixtures of a carburizing compound containing 80% of oak-wood charcoal and 20% of barium carbonate, at 900° C. in the transparent silica vessel shown in Fig. 1, measuring 3 cm. in dia. \times 15 cm. long. After approximately $2\frac{1}{2}$ hr. at temperature a very small sample of gas, amounting to no more than 2–3 c.c. at N.T.P., was extracted from a point near the specimen by means of the small sampling tube arranged alongside it. The sampling tube consisted of a very small quartz bulb, approximately 2 cm. in dia., connected directly to a length of quartz capillary stemming from which it was isolated by means of a tap. The extreme end of the stemming was blown out

into a very small thin-walled bulb, and the whole was evacuated beforehand by a diffusion pump to a pressure of 10^{-5} mm. of mercury, and sealed off. The sampling tube was then placed in the carburizing container in such a position that the thin-walled bulb was located alongside the steel specimen and directly above the quartz rod shown in Fig. 1. The sample of gas for analysis was extracted by depressing the sampling tube so that the thin-walled bulb was pierced, and the stopcock on the tube was then opened. The temperature of the specimen was measured by means of a fine-wire thermocouple attached to it near the point at which the gas sample for analysis was extracted. The small volume of gas was analysed for carbon dioxide, carbon monoxide, and hydrogen, on a diffusion-pump analytical system such as is used for the extraction and analysis of gases in metals (Fig. 2) and which has been described in detail by Ransley.⁹ It is considered that the relative concentrations of the oxides of carbon were not materially changed during the sudden withdrawal of the gases into the sampling tube, and that the analyses given in Table I. are typical of those actually existing in the carburizing box.

TABLE I.—Composition of Gas Extracted from Carburizing Box.

Carburizing temperature: 900° C. Steel: 3% nickel case-hardening. Carburizing compound: 80% oak-wood-charcoal/20% barium-carbonate.

Test No.	CO ₂ , %.	CO, %.	H ₂ , %.	Ratio CO ₂ /CO.
1	0.8	30.6	14.9	0.026
2	0.9	35.6	16.2	0.025
3	1.2	32.3	17.0	0.037

The temperature-equilibrium relationship for the iron/carbon-monoxide/carbon-dioxide system is shown in Fig. 3, from which it will be noted that at 900° C. the ratio of CO₂/CO for equilibrium with saturated austenite is 0.020. According to Becker,¹⁰ the CO₂/CO equilibrium ratio at 900° C. with respect to solid carbon is 0.029. The concentration ratio of these constituents in the gases extracted from the carburizing box tends to fall between the equilibrium values for saturated

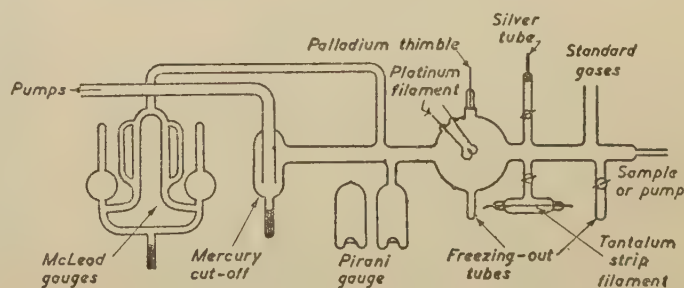


FIG. 2.—Apparatus for the Micro-Analysis of Gases.

austenite and solid carbon, and unless the excess of carbon dioxide is removed from the proximity of the steel surface, as, for example, by preferred absorption on the charcoal, carburization by the carbon monoxide alone to give saturated austenite is not possible. The other feature of the analysis

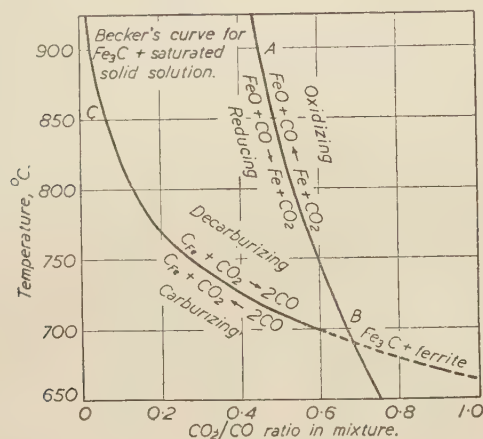


FIG. 3.—Equilibrium for the Systems Fe-C_{Fe}-FeO-CO-CO₂.

given in Table I. is the high concentration of hydrogen in all of the gas samples extracted. The charcoal used in the manufacture of carburizing compounds is highly porous, and there is no doubt that in general such mixtures contain quite high concentrations of absorbed water vapour before use. Evaporation of the water from the charcoal expels most of the air originally occluded in the box, and it is suggested that the main source of the atmosphere in the box is the reactions between water vapour and hot carbon:



It is considered that the hydrogen thus formed plays quite an important rôle in the process, either by cleaning up adsorbed films of CO₂ or by the cyclic formation of hydrocarbons by direct reduction either by the charcoal or by the oxides of carbon:



That hydrogen in the presence of carbon monoxide increases the rate of carburization has already been demonstrated by Bramley,⁷ and, as will be shown later, generated atmospheres similar in composition to those found in a carburizing box and shown in Table I. have given a rate of carburization superior to that obtained under comparable conditions in carbon monoxide, and comparable to that resulting from pack-carburizing.

Gas-Carburizing.

In gas-carburizing processes the carbon is supplied by the decomposition of a gaseous carbon compound which is either thermally unstable at the temperature of treatment or is present in excess of its equilibrium concentration with respect to the products of its dissociation. Thus in the case of methane, it is necessary to consider the equilibrium relationship for the reaction (5) to ensure that at the temperature of treatment the methane concentration is in excess of the equilibrium value with respect to hydrogen, in order that carburization may be promoted by the decomposition of the excess of the hydrocarbon (see Fig. 4). Hydrocarbons such as propane and butane, however, are thermally unstable above approximately 500–600° C. and tend to dissociate to the basic methane, setting free nascent carbon which is either absorbed by the steel or collects as sooty deposit:



The end product, methane, is also a carburizing gas, although its rate of decomposition is comparatively slow. Hydrocarbon gases are reducing and, provided that the rate of deposition of the

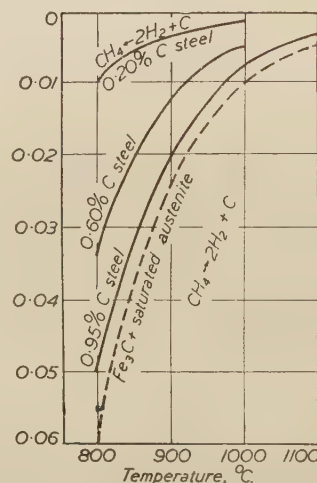


FIG. 4.—Equilibrium for the System Fe-C_{Fe}-CH₄-H₂ (Sykes).

carbon does not exceed that at which the carbon is absorbed by the steel, clean carburized work should be obtained. The degree of sooting is determined by the concentration of the hydrocarbon in the carburizing atmosphere and this may be reduced by dilution with suitable media, such as air or a prepared burnt fuel gas. Dilution of the hydrocarbon in this way reduces the tendency to sooting by promoting reactions between the decarburizing gases, such as carbon dioxide, water vapour, hydrogen, and oxygen, and the hydro-

carbon gas or the deposited soot. The concentrations of the decarburizing gases thus influence the sooting tendencies of the carburizing atmosphere, but precautions must be taken to ensure that decarburization of the steel is not also obtained. Conditions for non-sooting are also affected by the temperature of treatment and by the nature of the steel, particularly in regard to alloy additions; for example, nickel catalytically promotes the decomposition of hydrocarbons at elevated temperatures. In continuous electric furnaces, where the heating elements may be exposed to the carburizing atmosphere, the excessive accumulation of soot on the elements may lead to attack of the resistors and to short circuits, whilst refractory furnace linings may disintegrate owing to the

the metal surface, and atomic diffusion of the elements comprising the molecule may take place. Thus, in the case of carburization by carbon monoxide, the primary reaction is the dissociation of the molecule of the gas at the surface into free carbon and oxygen atoms, the former being readily absorbed by the steel at the carburizing temperature. Oxygen diffuses at a slower rate than carbon, so that most, if not all, of the atoms of this gas left free on the surface of the steel combine with another molecule of carbon monoxide or of any other reducing gas present. Some absorption of oxygen may also be obtained, especially in solid carburizing, but in atmospheres free from oxygen-containing gases, the reaction at the surface of the steel is solely that of adsorption and diffusion of the atomic carbon set free by the dissociating gas.

III.—EXPERIMENTAL.

Materials and Apparatus Used.

The following three representative case-hardening steels were used for the experiments :

- Low-carbon case-hardening steel (0.15% carbon).
- 3% nickel case-hardening steel (0.16% carbon, 3.17% nickel, 0.07% chromium).
- Nickel-chromium case-hardening steel (0.13% carbon, 3.18% nickel, 1.10% chromium).

In the majority of the experiments the steel being carburized was in the form of round bars 150 mm. long, turned down accurately between centres from 12.5 to 10 mm. dia. in order to remove any decarburized skin. The bars were ground to a smooth and bright surface finish. Flat mild-steel plates, 40 × 12 × 3 mm. thick, ground to a smooth finish on No. 0 emery cloth, were used for a limited series of experiments with butane and with a specially treated burnt-town's-gas

atmosphere. Before treatment every specimen was degreased in acetone and dried in ether, and the increase in weight resulting from the carburization was related to the surface area of the specimen.

Carburization of the flat mild-steel plates was carried out in a butt-ended silica tube, $\frac{3}{4}$ in. in dia., heated in a thermostatically controlled vertical-tube furnace (Fig. 5(a)). The steel specimen was suspended freely from the head of the tube, which could be removed from the furnace for quick cooling. Carburizing gas was introduced near the bottom of the reaction tube, just below the specimen, and was led off and burnt at the top of the tube, the gas flow being indicated on a suitable orifice gauge.

For experiments on the round bars, use was

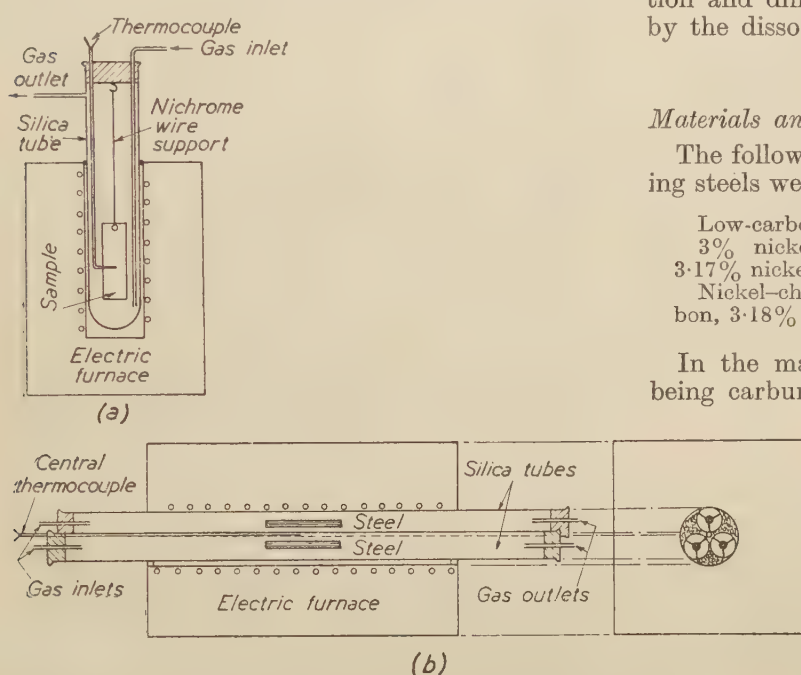


FIG. 5.—Furnaces for Gas-Carburizing Experiments.

precipitation of carbon in the pores of the bricks. Sooting of the work being treated can also adversely affect the uniformity of the carburization, and may even suppress the reaction completely.

Finally, in the consideration of any gas-carburizing process it is necessary to bear in mind that carburization is essentially a surface-reaction process. Irrespective of the nature of the carburizing gas, the atomic or nascent carbon is produced at the surface of the iron and not internally by the decomposition of the gas after diffusion. Researches into gas-metal reactions and diffusion processes have shown that a complex molecule is incapable of diffusion through a solid metal, except through large rifts or like defects in the structure. It may dissociate, however, into its individual atoms upon adsorption on

made of a horizontal tube furnace accommodating three silica tubes, each of $\frac{3}{4}$ in. internal dia., and thus three tests could be carried out simultaneously at a constant temperature, under different conditions of gas flow or time of treatment, &c. (Fig. 5(b)). The furnace was thermostatically controlled to within $\pm 3^\circ$ C. of the required temperature, and in all tests the direction of the flow of gas over the specimen was reversed half-way through the carburization period. In order to ensure uniformity of carburization, the steel specimen was located centrally in the furnace tube on a silica support, which gave only point contact with the steel.

The carburizing properties of two types of atmospheres, namely, the hydrocarbon-rich type and that containing little or no hydrocarbon gas and approximating to the atmosphere which, as shown above, is to be found in a pack-carburizing box, have been investigated. The hydrocarbon-containing gases have included town's gas, butane, and propane, and a study has been made of the effect of diluting these gases with inert or decarburizing agents for the purpose of reducing sooting of the work, whilst maintaining a high rate of carburization. The carburizing atmospheres not containing hydrocarbons were specially prepared in generators typical of those used industrially for controlled-atmosphere production. The following is a summary of the various carburizing and diluting atmospheres used in the experiments:

Carburizing Gases.

- (a) Town's gas.
- (b) Butane.
- (c) Propane.
- (d) Partly burnt town's gas, reheated over hot charcoal.
- (e) Rich town's gas/air mixtures pretreated over hot charcoal.
- (f) An atmosphere produced by the action of steam on hot charcoal.

Diluting Gases.

- (a) Air.
- (b) Partly burnt town's gas.
- (c) Partly burnt town's gas, reheated over hot charcoal.

The temperature of carburization selected was, in the majority of the tests, typical of industrial practice for the steel in question. Thus, whilst the carburization of the mild steel in the partly burnt town's gas atmosphere, pretreated over hot charcoal, was studied at temperatures ranging from 750° to 950° C., the work with hydrocarbon-containing atmospheres was carried out at 925° C. Both the alloy steels were carburized at 900° C. Among the factors studied were the composition of the carburizing atmosphere, the rate of flow of the carburizing gas, the time of treatment, and

the surface condition of the steel before carburization.

Evaluation of the Degree of Carburization.

The degree of carburization was determined in a number of ways: (1) By measurement of the increase in weight of the steel per unit area of surface; (2) by chemical determination of the carbon content of the marginal layers of the carburized steel; (3) by metallographic estimation of the depth of the case; and (4) by depth-hardness measurements on the quench-hardened carburized steel.

Chemical analysis of samples turned off the steel surface gave the average carbon content over a depth of 0.005 in. Before turning, the surface was lightly polished with fine emery to remove any films of oxide or free carbon. For accurate analysis it is necessary to have a sufficient weight of sample for duplicate tests, and this may be obtained only from a specimen of sufficient diameter or length. In the experiments described in this paper, these conditions have been fairly well satisfied, and the analyses quoted in the tables are considered to be accurate to within 0.005% of carbon. On the other hand, the results lose a little of their significance because of the difficulty encountered in taking accurately measured cuts from bars which may have warped slightly in carburizing. In this respect the results are taken to be representative of the average carbon content of a marginal zone 0.004–0.006 in. deep.

Hardness measurements on a taper-ground, quenched specimen serve to illustrate both the surface carbon content and the depth of case. However, the test is liable to error, mainly associated with the method and the efficiency of the quenching operation, and it is influenced considerably by the nature and size of the test-specimen. The human element has probably a much greater effect on the results obtained by this method of test than on those obtained by any other of the methods described, and the test has not been used to any great degree during this investigation.

Metallographic examination of the carburized and non-hardened steel gives a very satisfactory, though approximate, indication of both the surface carbon content and the depth of case, and reveals any inequalities in the carburization which are not shown by the other methods of examination. The accurate determination of the case-core boundary is difficult, however, since it is not sharply defined. Accordingly, the case depths quoted in the paper are those measured to a depth at which the estimated carbon content of the steel is of the order of 0.3–0.4%. Estimation of the surface carbon content by metallographic examination necessitates reference to standard

structures of known carbon content and can therefore be only approximate.

The change-in-weight method can be carried out with great accuracy provided that the surface of the specimen is not contaminated by oxide and/or free carbon. In experiments described in this paper many of the test-specimens were either oxidized or sooted. In the latter case, the excess of soot was brushed off, leaving merely a thin adherent film of negligible weight, which introduced an error considered not to exceed 1%. Specimens which were oxidized after treatment were heated in dry hydrogen at 600° C. before weighing. This treatment reduced the oxide film without giving rise to decarburization. The change-in-weight method serves as a very valuable guide to the degree of carburization (or decarburization) and as a comparative method of test is probably superior to any other.

It is not possible to present a complete picture of the degree of carburization obtained under particular conditions of treatment by using only one of the above methods of test; it is necessary, if full data are required, to follow the progress of cementation by at least two of these methods.

IV.—CARBURIZATION WITH TOWN'S GAS AND WITH BUTANE.

Carburization in Town's Gas.

Town's gas has been experimented with and tried on a commercial scale for many years as a carburizing medium, with varying degrees of success. In order to increase its carburizing power, the gas has in some cases been enriched with a hydrocarbon such as propane or petrol vapour and satisfactory results have been reported.¹¹ Guthrie and Wozasek¹² have noted the variable carburization obtained with town's gas supplies, of seemingly identical composition, coming from different sources. Dehydration of the gas, followed by addition of a fixed concentration of water vapour, was found to lead to more consistent results, and it was suggested that the presence of an oxygen-containing gas is necessary for efficient carburization, in order to prepare the steel surface by alternate oxidation and reduction. Wilbor and Comstock¹³ attempted to control the carburization so as to balance dissociation of the hydrocarbons in town's gas against the rate of absorption of carbon by the steel. It was considered that in the main carburization proceeds *via* the dissociation of unsaturated hydrocarbons, the breakdown of which may be restrained by the application of pressure.

The carburization of mild steel in town's gas as delivered from the mains has been investigated. Case depths of the order of 0.007 in./hr. for treatments up to 5 hr. at 925° C. were obtained, but the results on the whole were very inconsistent.

Carburization was always accompanied by fairly heavy sooting of the steel, which resulted in non-uniformity in the depth and carbon content of the case, and in some instances carburization was prevented altogether. This is illustrated in Fig. 11, which shows a section of a specimen, one surface of which has been carburized to some depth. The opposite face, however, has been sooted to

TABLE II.—*Carburization of 0.15% Carbon Steel at 925° C. for 5 Hr. in Town's-Gas/Burnt-Town's-Gas Atmospheres.*

Town's gas: 2.6% CO₂, 2.4% C₂H₄, 11.0% CO, 21.5% CH₄, 56.0% H₂, 2.0% H₂O, 4.5% N₂.
Burnt town's gas: 4.7% CO₂, 9.1% CO, 14.7% H₂, 0.6% CH₄, 68.6% N₂, 2.3% H₂O.

Carburizing Atmosphere.		Weight Increase, mg./sq. mm. × 10 ³ .	Case Depth, in.	Comments.
Town's Gas, %.	Burnt Town's Gas, %.			
100	0	37.5	0.037	Heavy soot. Adherent. Non-uniform case.
75	25	31.3	0.032	Heavy soot. Adherent surface deposit. Non-uniform case.
50	50	27.2	0.030	Light soot. Readily brushed off. Uniform case.
25	75	19.2	0.017	Very light soot. Readily brushed off. Uniform case.
10	90	2.1	Trace	No soot.

such a degree that carburization has been practically inhibited.

Dilution of town's gas with partly burnt town's gas decreases the amount of sooting, though only at the expense of a serious reduction in the rate of carburization (*see* Table II.). This is due to the fact that whilst town's gas contains some very strong carburizing constituents in the form of

TABLE III.—*Carburization in Purified Town's Gas.*

Analysis: 9.0% CO, 52.5% H₂, 20.1% CH₄, 18.5% N₂.

Steel.	5 hr. at 925° C.		5 hr. at 1000° C.	
	Weight Increase, mg./sq. mm. × 10 ³ .	Case Depth, in.	Weight Increase, mg./sq. mm. × 10 ³ .	Case Depth, in.
Mild steel . . .	56.0	0.060	86.0	0.080
Nickel steel . . .	43.6	0.040	77.8	0.060
Nickel-chromium steel	80.1	0.076

hydrocarbons, it is reduced to the status of only a mildly carburizing gas by the presence of decarburizing agents such as water vapour, carbon dioxide, and hydrogen. It will be noted

that increasing additions of the partly burnt town's gas reduce, and eventually completely neutralize, the carburizing power of the raw town's gas.

Removal of the decarburizing gases from raw town's gas results in a very strongly carburizing atmosphere, as shown in Table III. Town's gas as received was passed through the following purification train: Activated carbon, for the removal of sulphurous gases; charcoal, maintained at 750° C., for the removal of the oxygen and for the breakdown of the unsaturated hydrocarbon gases; caustic potash for the absorption of the carbon dioxide; and an activated alumina drier.

The composition of the purified gas was as follows:

Carbon monoxide	9%
Hydrogen	52.5%
Methane	20.1%
Nitrogen	18.5%
Carbon dioxide	—
Oxygen	—
Water vapour	—
Hydrocarbons	—

The specimens of mild steel carburized at 925° C. in this atmosphere were covered with a light film of soot, whilst those treated at 1000° C. were sooted at both ends. The rate of carburization obtained was extremely good and was superior to that typical of pack-carburizing practice.

Carburization with Butane.

Experiments with pure butane resulted in the rapid sooting-up of the reaction tube, so that even

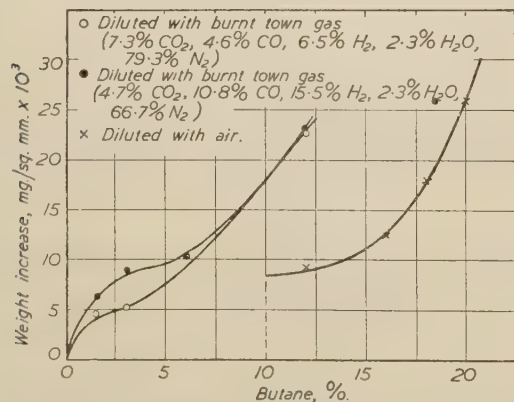


FIG. 6.—3.17% Nickel, 0.16% Carbon Steel Carburized in Diluted Butane at 900° C. for 5 hr.

at very low gas velocities the passage of the hydrocarbon gas through the tube was stopped completely after a very short time. Further tests were carried out with butane diluted with air or with partly burnt town's gas, the experiments being limited to the 3% nickel steel treated at 900° C. for a period of 5 hr. and in a gas flow of 0.7 linear ft./min. (Fig. 6). In all tests sooting was ex-

cessive, although dilution with burnt town's gas effected some slight improvement in this respect. It was not possible to reduce the concentration of butane sufficiently to eliminate sooting, without also suppressing completely the carburizing reaction. Much of the soot deposit was loose and could be readily brushed off the specimen, leaving the surface covered with a thin adherent coating of carbon. Specimens treated in air-butane mixtures had, in addition, a thin oxide coating. The heavy sooting associated with the carburization in dilute butane atmospheres leads to non-uniformity of carburization, the effect being very similar to that obtained with raw town's gas and illustrated in Fig. 11.

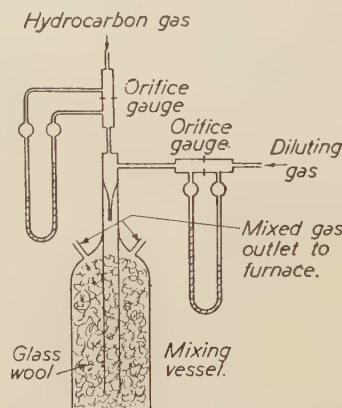


FIG. 7.—Apparatus for Mixing Gases before Entry to Electric Furnace.

V.—CARBURIZATION WITH DILUTED PROPANE.

Carburization in Air-Propane Atmospheres.

Propane is available commercially as "Propa-gas" and may be obtained in cylinders or tanks in which it is liquefied under pressure, 1 lb. of liquid propane giving approximately 8 cu. ft. of gas at N.T.P. In view of the results obtained with town's gas and undiluted butane, no experiments have been carried out with the raw propane gas, but a considerable study has been made of the carburizing properties of diluted propane atmospheres. The gas, having the formula C_3H_8 , is a lower member of the methane series than is butane (C_4H_{10}), and has therefore less carbon available for sooting at elevated temperatures. The experiments with this gas have in the main been associated with the elimination of sooting by dilution of the hydrocarbon with media such as air or a controlled atmosphere, whilst maintaining the maximum possible rate of carburization.

Controlled volumes of propane and of air were lead into a small mixing vessel packed with glass wool as shown in Fig. 7 and thence to the furnace tubes. Carburization of the plain carbon steel and the two alloy steels was carried out at the appropriate temperatures in atmospheres con-

TABLE IV.—*Carburization of Steels in Air-Propane Atmospheres.*

Rate of gas flow : 5 ft./min.

Propane, %.	Time, hr.	0.15% C Steel at 925° C.			3.17% Ni, 0.16% C Steel at 900° C.			3.18% Ni, 1.1% Cr, 0.13% C Steel at 900° C.		
		Weight In- crease, mg./sq. mm. $\times 10^3$.	Surface Carbon Content, %.	Case Depth, in.	Weight In- crease, mg./sq. mm. $\times 10^3$.	Surface Carbon Content, %.	Case Depth, in.	Weight In- crease, mg./sq. mm. $\times 10^3$.	Surface Carbon Content, %.	Case Depth, in.
20	2½	10.0	0.38	0.007	4.5	0.16	...	10.0	0.57	0.025
20	5	13.1	0.41	0.015	5.5	0.18	...	12.6	0.58	0.033
20	10	21.3	0.50	0.024	7.0	0.21	...	19.5	0.64	0.043
24	2½	15.0	0.65	0.020	10.2	0.35	0.010	15.0	0.60	0.028
24	5	25.6	0.90	0.030	14.6	0.58	0.018	17.6	0.66	0.038
24	10	38.0	1.06	0.040	23.2	0.88	0.033	23.7	0.70	0.050
28	2½	23.0	0.85	0.027	16.2	0.65	0.020	19.5	0.69	0.034
28	5	38.5	0.94	0.038	21.5	0.76	0.030	22.3	0.74	0.042
28	10	61.7	1.12	0.058	41.2	1.05	0.038	29.2	0.84	0.060
32	2½	32.8	0.96	0.032	22.1	0.87	0.024	24.5	0.70	0.038
32	5	50.5	1.10	0.055	30.4	0.88	0.033	27.1	0.76	0.047
32	10	69.8	1.21	0.079	45.1	1.01	0.042	35.5	0.85	0.064

taining 16–32% of the hydrocarbon, and for periods up to 10 hr. The results are summarized in Table IV. and Fig. 8. Photomicrographs and macrographs of the case depth obtained at the optimum conditions of treatment are shown in Figs. 9(a) and 10(a).

Under any given conditions the maximum case depth was obtained with the nickel-chromium alloy steel, whilst the nickel steel was found to give the lowest penetration of the three steels studied. It will be seen from Table IV., that as the concentration of the hydrocarbons in the carburizing atmosphere increases, so the surface concentration of carbon in the steel increases, indicating the changing equilibrium conditions as the composition of the atmosphere is varied. Increasing the concentration of propane above approximately 30% has little effect upon the carbon content of the case or its depth. This is probably associated both with the heavy soot deposits which form in atmospheres containing high concentrations of propane, and with the fact that the rate of supply of nascent carbon to the steel equals the rate of absorption. The concentration of propane necessary to reduce sooting to a negligible quantity varies somewhat with the temperature of carburization, but at the same time the atmosphere is not strongly carburizing and is suitable only for the production of light cases of medium carbon content. For heavy cases, rich propane-air mixtures must be used, which lead to sooting and to a certain lack of uniformity of case depth. Sooting was excessive with hydrocarbon contents above approximately 25%, and control over the carburization was not absolute. The surface concentration of carbon, which in the case of the plain car-

bon steel exceeded the eutectoid composition, as well as the case depth, were both rather greater than those obtained in a solid carburizing compound under comparable conditions of test.

The explosive limits for air-propane mixtures are narrow, and lie within the range 2–9.5% of propane, but mixtures which give the maximum rate of carburization are well outside this range. Dilution with air is inexpensive and reduces the soot-forming tendency of the pure gas by combustion of a major portion of the propane added, thus in effect producing a complex atmosphere of the oxides of carbon, water vapour, nitrogen, hydrogen, and excess hydrocarbon. Some of the soot deposited from the latter is removed by direct reaction with the decarburizing gases generated in the furnace chamber, whilst the simultaneous reduction in the concentration of the hydrocarbons by the combustion, also decreases the

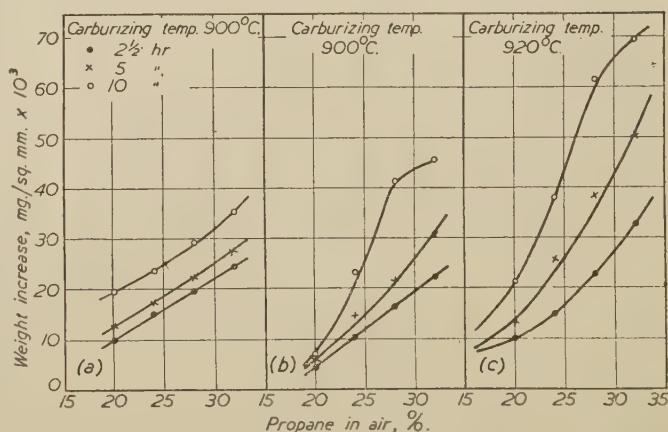


FIG. 8.—Carburization in Propane-Air Mixtures of Steels Containing (a) 3.18% Ni, 1.10% Cr, and 0.13% C, (b) 3.17% Ni and 0.16% C, and (c) 0.13% C.

TABLE V.—*Carburization of Steels in Burnt-Town's-Gas-Propane Atmospheres.*

Burnt fuel gas : 4.8% CO₂, 10.8% CO, 15.6% H₂, 2.3% H₂O, 66.6% N₂.
Rate of gas flow : 5 ft./min.

Propane, %.	Time, hr.	0.15% C Steel at 925° C.			3.17% Ni, 0.16% C Steel at 900° C.			3.18% Ni, 1.1% Cr, 0.13% C Steel at 900° C.		
		Weight In- crease, mg./sq. mm. × 10 ³ .	Surface Carbon Content, %.	Case Depth, in.	Weight In- crease, mg./sq. mm. × 10 ³ .	Surface Carbon Content, %.	Case Depth, in.	Weight In- crease, mg./sq. mm. × 10 ³ .	Surface Carbon Content, %.	Case Depth, in.
20	2½	29.5	0.92	0.027	13.2	0.37	0.010	10.0	0.52	0.027
20	5	40.7	1.11	0.037	16.5	0.47	0.017	13.5	0.54	0.037
20	10	64.5	1.22	0.055	23.0	0.59	0.027	17.5	0.59	0.050
24	2½	30.2	1.08	0.035	16.2	0.58	0.017	11.4	0.52	0.033
24	5	43.7	1.09	0.050	23.1	0.68	0.028	15.1	0.59	0.045
24	10	72.0	1.19	0.068	31.7	0.77	0.034	21.3	0.66	0.055
28	2½	31.5	0.98	0.038	18.6	0.64	0.023	12.5	0.56	0.036
28	5	46.6	1.17	0.057	26.9	0.78	0.032	16.5	0.63	0.048
28	10	73.3	1.22	0.078	32.0	0.83	0.040	22.4	0.71	0.058
32	2½	31.9	1.10	0.040	19.2	0.66	0.026
32	5	50.5	1.20	0.062	27.3	0.79	0.035
32	10	74.7	1.23	0.083	32.5	0.85	0.046

amount of soot that is formed. At the same time, however, the carburizing power of the mixture is decreased, and with increasing dilution the concentration of the decarburizing gases formed by the combustion calls for an ever-decreasing equilibrium concentration of carbon in the surface of the steel.

Carburization in Burnt-Town's-Gas-Propane Atmospheres.

Dilution of propane, either by a furnace flue gas or by a controlled atmosphere specially prepared in a generator by the controlled combustion of a fuel gas, also results in a reduction in the sooting accompanying carburization. In effect, a carburizing mixture is produced which is similar to that obtained by dilution of propane with air, but in this case it has the advantage of being under stricter control.

A series of experiments similar to those with air-propane mixtures were carried out with propane diluted with partly-burnt town's gas, the composition of which is given, together with a summary of the results, in Table V. The structure and depth of the case obtained are illustrated in Figs. 9(b) and 10(b) which show respectively the micro- and macrostructures of mild steel after carburization. Fig. 12 shows the effect of time on the nature and depth of the case obtained on the nickel-chromium steel carburized in a 28% propane-72% burnt-town's-gas mixture.

As in the case of dilution with air, a concentration of propane in excess of 30-32% did not materially improve the rate of carburization, and above about 25% of propane sooting was excessive. But on the whole, under comparable

conditions of cementation, the sooting was less than in air-propane mixtures. Sooting was never completely eliminated, however, when cases of high carbon concentration were required, and in general the reduction in the amount of sooting with increasing dilution was not so marked as that obtained by similar dilution with air. The decarburizing gases present in the burnt town's gas tend to offset the carburizing and sooting properties of propane, and by control over the amount of the hydrocarbon added the type of case can be varied to suit requirements. Too high a concentration of carbon dioxide, or in other words a high combustion ratio of air to town's gas in the atmosphere generator, was found to give inconsistent and irregular cases, owing to the strong decarburizing properties of the dioxide. It is considered that the concentration of the carbon dioxide in such atmospheres used for carburizing work should not exceed 5%.

From the results for mild steel, it appears that burnt-town's-gas-propane mixtures are more effective carburizers than air-propane mixtures of similar hydrocarbon content. However, in the case of the alloy steels, this is not so. It is probable that this difference is due to the fact that when the alloy steels were treated in the burnt-town's-gas-propane atmosphere, the soot produced was in the form of a dense shell which could in some instances be removed as a tube from the cylindrical specimens. This hard carbon deposit formed a compact case around the steel and reduced the rate of carbon absorption. The difference in the nature of the soot deposits was probably associated with the catalytic activity of the different steels in promoting the rapid pyrolysis of the hydrocarbon.

Table VI. summarizes the results on the effect of the linear rate of flow of the carburizing gas upon the degree of carburization obtained. Below 2.0 linear ft./min. there was a slight

TABLE VI.—*Effect of Rate of Flow of Atmosphere on the Carburization of Steel.*

Steel: 3.17% Ni, 0.16% C. Temperature: 900° C.
Time: 5 hr.
Diluting gas: 4.8% CO₂, 10.8% CO, 15.5% H₂, 2.3% H₂O, 66.6% N₂.

Gas Flow, ft./min.	Carburizing Atmosphere.	Weight Increase, mg./sq. mm. × 10 ³ .	Surface Carbon Content, %.	Case Depth, in.
1	20% propane-80% burnt-town's-gas.	11.8	0.36	0.010
2		14.7	0.40	0.013
3		16.6	0.46	0.018
5		16.5	0.47	0.017
1	28% propane-72% burnt-town's-gas.	19.0	0.57	0.022
2		23.0	0.70	0.028
3		25.6	0.75	0.030
5		26.9	0.78	0.032

decrease in the amounts of soot and oil-dissociation products formed. Above this rate of flow, there was very little increase in the rate of carburization.

Sooting in Diluted Propane Atmospheres.

Burnt town's gas is a complex mixture of oxidizing, reducing, carburizing, and decarburizing gases, diluted with the inert gas nitrogen. Of the active gases, carbon dioxide and water vapour are both oxidizing and decarburizing to steel of more than low-carbon quality; carbon monoxide and methane are both reducing and carburizing; hydrogen is reducing and mildly decarburizing, and stimulates the decarburizing power of carbon dioxide and water vapour, in particular, by maintaining an oxide-free steel surface. Except at air/town's gas combustion ratios below about 1½:1, burnt town's gas is decarburizing to all carbon steels above 725° C., the unburnt fuel gas itself being only a mildly carburizing agent.

When propane is diluted with air for the purpose of carburizing, some of the hydrocarbon is used up almost immediately by combustion with the oxygen, giving combustion products comparable in nature and in relative concentrations with those comprising a partly burnt town's gas. The remaining unburnt propane may be considered, therefore, as fulfilling two functions: Part is utilized in the neutralization of the decarburizing gases generated in the primary combustion, and the balance is then free for the carburization of the steel. Under such conditions the actual concentration of propane which is directly effective in promoting carburization is very small, and in a 70% air/30% propane mixture, for example, it is

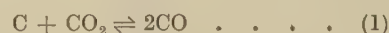
probably less than 5%. This type of atmosphere would be perfectly suitable for carburizing if the propane, which is consumed for purposes other than carburizing, were to be used up entirely by subsidiary reactions. In such a case air-propane mixtures would be ideal carburizing media, in that the use of an atmosphere generator for the production of the diluting gas would be avoided. Propane is unstable, however, above approximately 550° C., especially when in contact with metallic surfaces, and much of it dissociates into methane and carbon before the combustion and subsidiary inter-gas neutralizing reactions can take place:



Some of the carbon thus deposited enters into solution in the steel immediately on being set free, provided that the temperature is in excess of approximately 750° C., but much remains as a surface deposit that is comparatively non-reactive with the decarburizing gases which may be present. The deposition of soot results in a loss both in the potential neutralizing and in the carburizing powers of the propane added to the diluting gases, with the result that the concentration of hydrocarbon necessary to effect satisfactory carburization is much greater than that theoretically required. With the resulting high concentration of propane necessary for maximum carburization, sooting is inevitably excessive.

However, if the diluting atmosphere is free from decarburizing gases, the sole function of the propane that is added is for carburizing. This results in a considerable decrease in the concentration of the propane necessary to effect a required degree of carburization, with a corresponding decrease in sooting. In addition, since the only reaction involved is that of carburization, the process is under much better control.

Diluting atmospheres free from active decarburizing gases may be obtained by the chemical processing of partly burnt fuel-gas mixtures, whereby the carbon dioxide is removed by absorption in a solvent capable of regeneration and the processed atmosphere is dried over a desiccant such as activated alumina. Alternatively, the burnt gases may be passed over charcoal heated to approximately 1000° C. to remove the carbon dioxide and water vapour by reaction with the hot carbon, according to the following reactions:



The atmosphere thus produced contains nitrogen and carbon monoxide, with a hydrogen content determined by the degree of combustion of the raw fuel gas, by the dew-point of the burnt gas

TABLE VII.—*Removal of CO₂ and H₂O from Burnt Town's Gas by Reaction with Hot Charcoal at 1025° C.*

Air/Town's Gas Ratio.	Composition of Burnt Town's Gas as Generated.				Composition of Burnt Town's Gas Treated over Charcoal at 1025° C.			
	CO ₂ , %.	CO, %.	CH ₄ , %.	H ₂ , %.	CO ₂ , %.	CO, %.	CH ₄ , %.	H ₂ , %.
2 : 1	3.8	10.8	1.71	17.1	...	20.4	0.80	21.28
2½ : 1	4.8	9.2	1.29	12.9	...	20.0	0.79	14.3
3 : 1	6.6	6.4	0.43	8.1	...	20.1	0.43	10.3
3½ : 1	9.4	2.4	0.14	5.9	...	20.4	0.12	6.1
4 : 1	10.6	1.0	...	1.2	...	20.8	0.10	1.9

before treatment over the charcoal, and by the water-vapour content of the charcoal used. Thus, by complete combustion of the fuel, drying the products over a gel, and predrying the charcoal, a final gas mixture may be obtained which contains less than 0.5% of hydrogen and approximately 20% of carbon monoxide, the balance being nitrogen. The range of atmosphere compositions which may be obtained in this way is shown in Table VII.

As will be shown later, the atmosphere produced in the manner described above is in itself carburizing, and only a small concentration of propane is needed to produce very strongly carburizing conditions. The possibility of sooting is thus considerably reduced, and under certain conditions may be prevented completely without impairing the efficiency of carburization.

Carburization in Charcoal-Treated Burnt-Town's Gas-Propane Atmospheres.

A series of experiments were carried out in order to determine the maximum concentration of propane which could be tolerated at any temperature before sooting was obtained, the diluting gas being burnt town's gas processed over hot charcoal. Specimens of mild steel measuring

approximately $20 \times \frac{3}{4} \times \frac{1}{8}$ in. were heated in a silica tube in which the steel was so located that a temperature gradient existed from the middle of the bar to each end. Temperature readings along the length of the bar were taken by means of a fine-wire thermocouple, the tip of which travelled in a groove cut centrally along the length of the bar. The carburizing gas was fed into the furnace tube *via* a silica manifold located directly above the steel, so that the atmosphere entered the reaction tube at approximately equal velocities at intervals of $\frac{1}{2}$ in. along the length of the steel bar. The carburizing gas was used only when the temperature conditions were stabilized, pure hydrogen being employed during both the heating and the cooling of the steel. In all cases the time of heating in the carburizing gas was limited to 2 hr. The results are shown in Fig. 13.

The experiments indicated that the composition of the charcoal-treated gas, and in particular its hydrogen content, has little bearing on the minimum temperature at which carburization is obtained without sooting. The direction of the gas flow relative to the steel appears to be of some importance. Direct impingement of the carburizing gas on the steel surface immediately on entering the reaction chamber promotes sooting at

TABLE VIII.—*Carburization of Steels in Charcoal-Treated Burnt Town's Gas and Propane.*

Analysis of diluting gas : 20.8% CO, 1.2% H₂, 78% N₂. Rate of flow : 5 ft./min.

Propane, %.	Time, hr.	0.15% C Steel at 925° C.			3.17% Ni, 0.16% C Steel at 900° C.		
		Weight Increase, mg./sq. mm. $\times 10^3$.	Surface Carbon Content, %.	Case Depth, in.	Weight Increase, mg./sq. mm. $\times 10^3$.	Surface Carbon Content, %.	Case Depth, in.
2	2½	33.8	1.09	0.029	28.9	0.82	0.027
2	5	42.8	1.20	0.044	40.2	1.00	0.038
2	10	51.2	1.28	0.068	48.0	1.11	0.047
3	2½	30.6	0.95	0.030
3	5	43.7	1.08	0.042
3	10	50.1	1.16	0.051
4	2½	44.4	1.19	0.034	33.2	1.04	0.032
4	5	54.2	1.25	0.054	44.1	1.13	0.042
4	10	66.4	1.34	0.076	51.0	1.16	0.054
6	2½	46.3	1.19	0.037
6	5	58.1	1.24	0.066
6	10	74.0	1.30	0.083

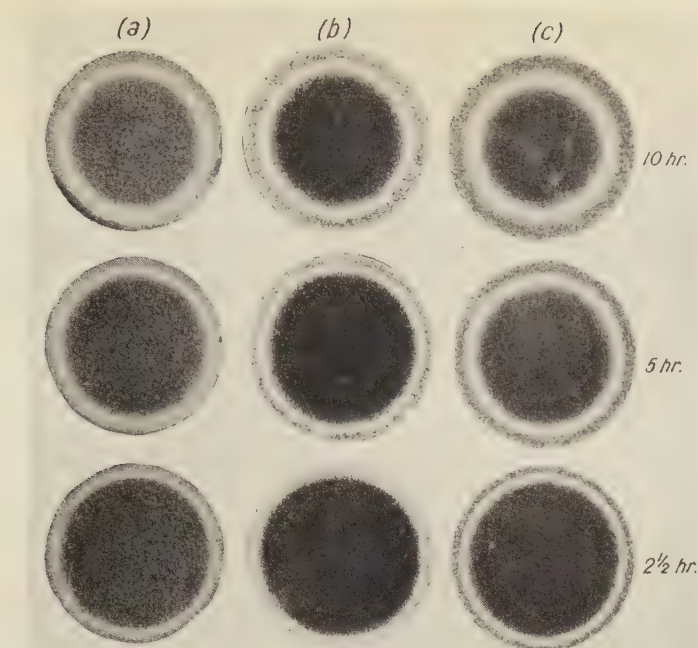


FIG. 9.—Effect of Carburizing Time on 0-15% Carbon Steel Carburized at 925° C. in (a) Air/Propane, (b) Burnt town's gas/Propane, and (c) Charcoal-treated gas/Propane. $\times 3$. (Reduced to four-fifths linear in reproduction.)

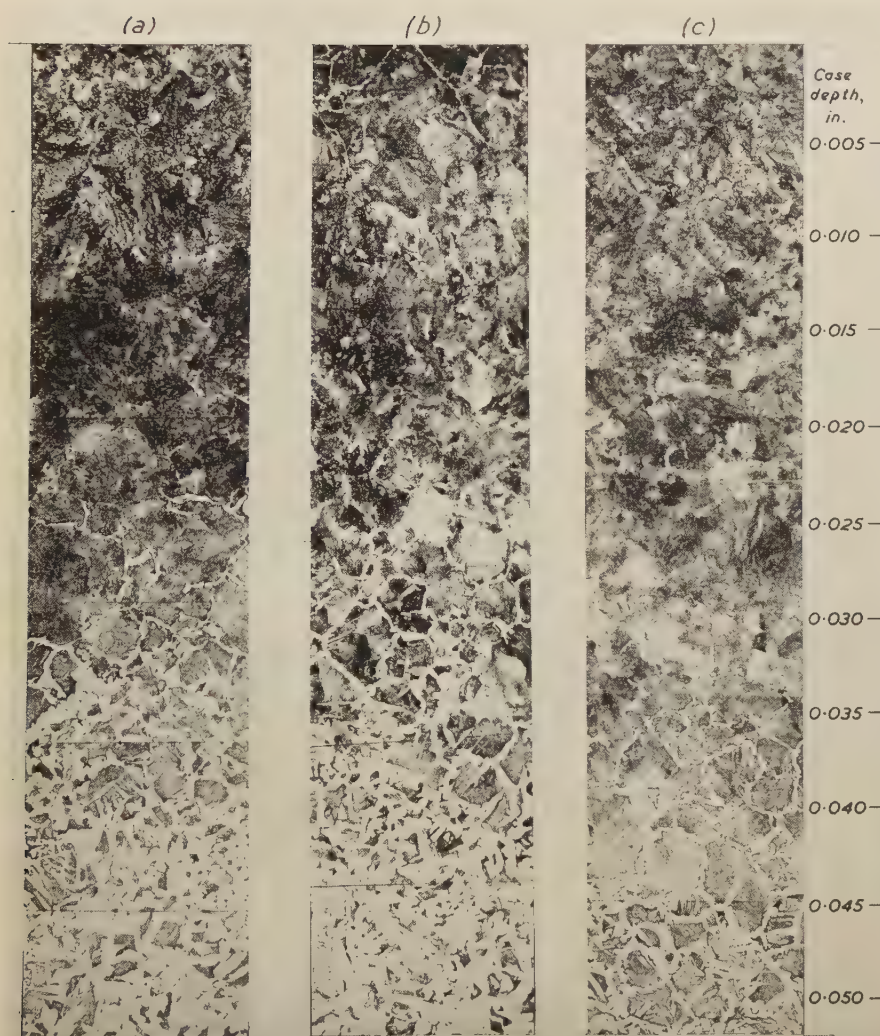


FIG. 10.—0-15% Carbon Steel Carburized at 925° C. for 5 hr. in (a) 28% Propane/72% Air, (b) 20% Propane/80% Burnt town's gas, (c) 4% Propane/96% Charcoal-treated burnt town's gas. $\times 200$. (Reduced to one-half linear in reproduction.)

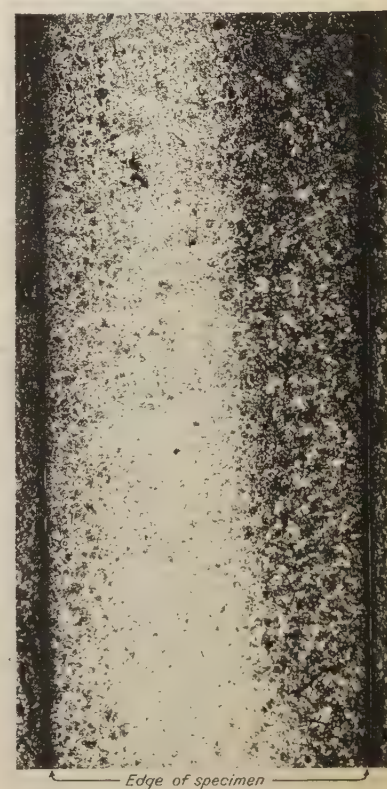


FIG. 11.—Mild Steel Carburized in Town's Gas, showing uneven case. $\times 20$. (Reduced to one-half linear in reproduction.)

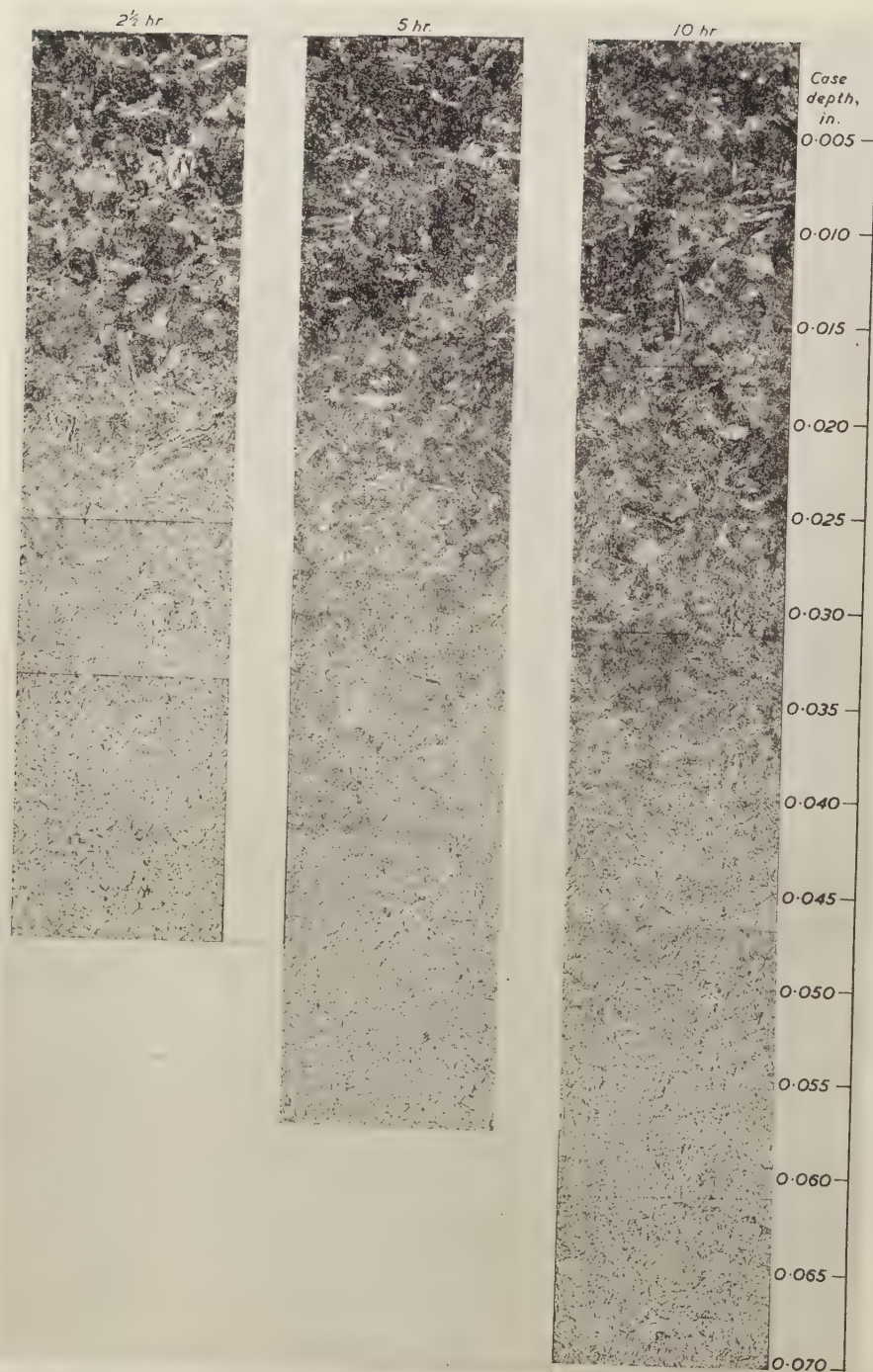
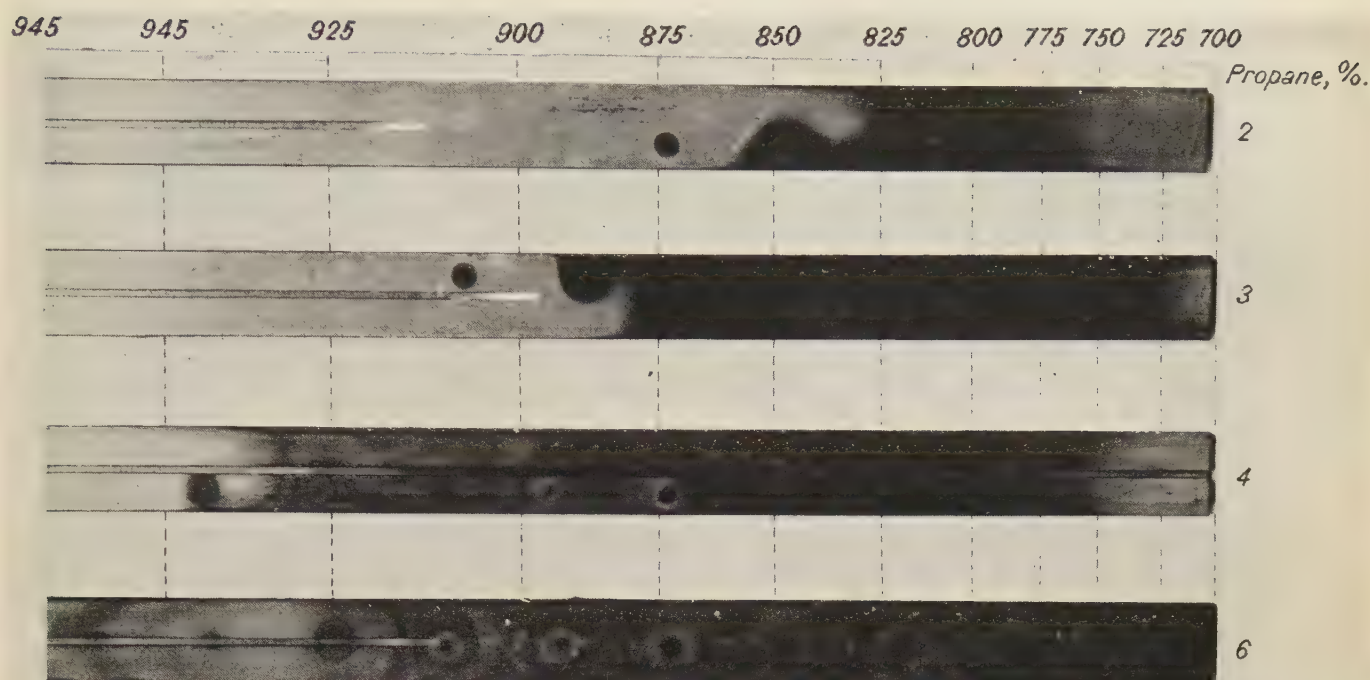
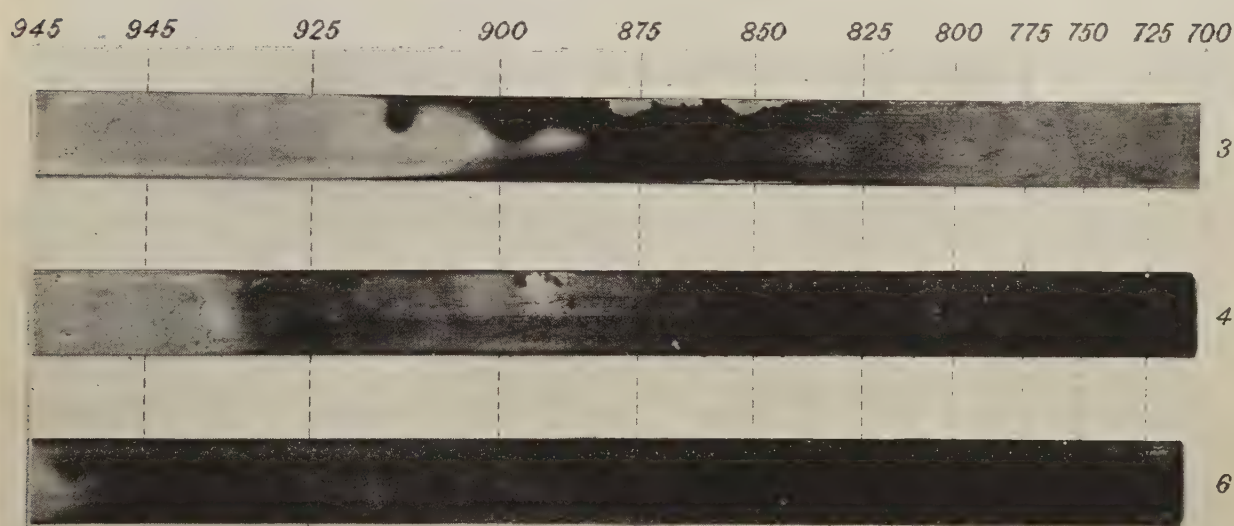


FIG. 12.—Effect of Carburizing Time on Nickel-Chromium Case-Hardening Steel. Carburized at 900° C. in 28% Propane/72% Burnt town's gas. $\times 200$. (Reduced to one-half linear in reproduction.)



Diluting gas: 19.8% CO; 14.7% H₂; 65.5% N₂.



Diluting gas: 20.8% CO; 1.2% H₂; 78.0% N₂.

FIG. 13.—Sooting of Mild-Steel Bars having a Temperature Gradient, on heating in propane and burnt town's gas preheated over hot charcoal.

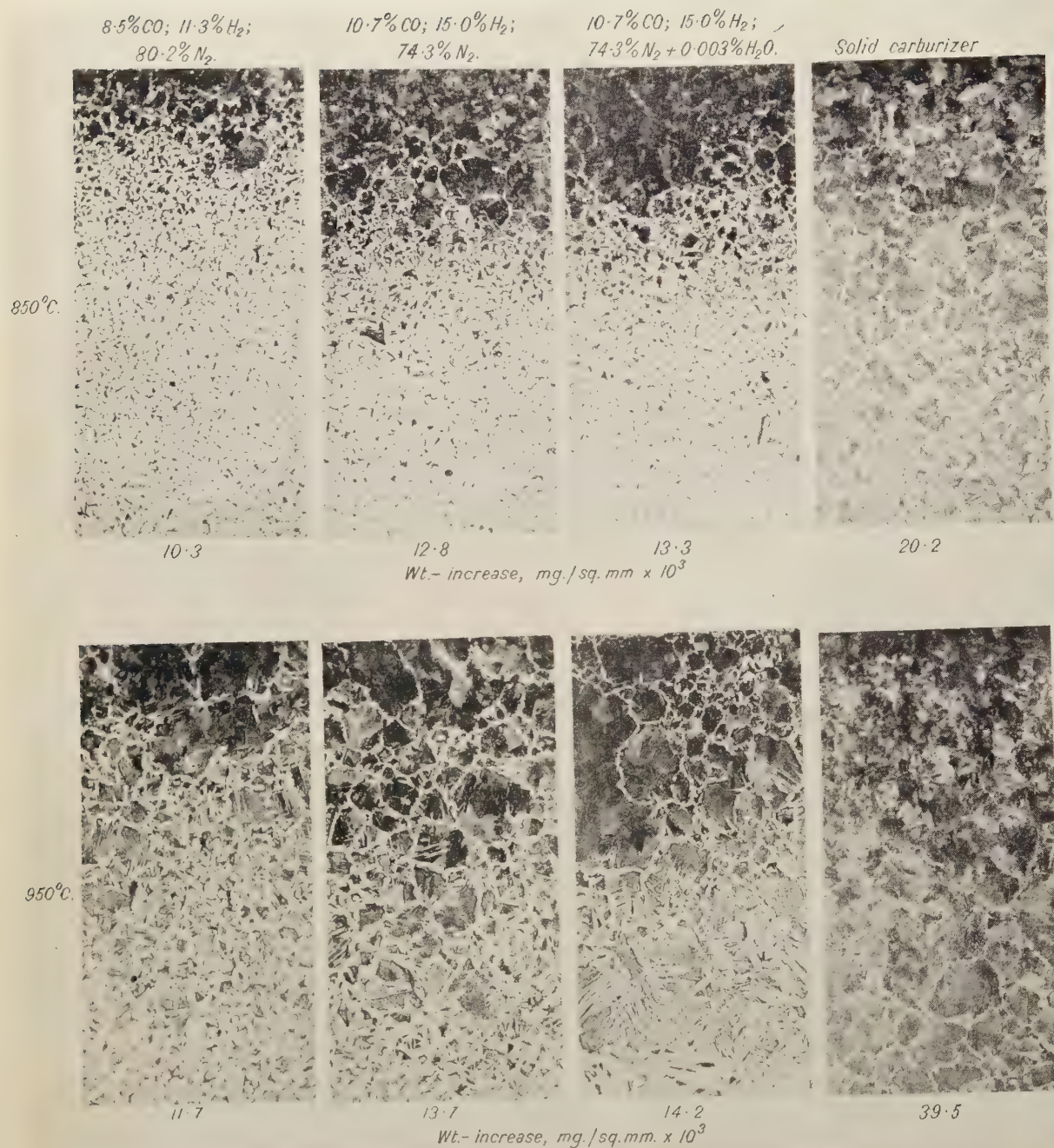


FIG. 14.—Mild Steel Carburized in Burnt Town's Gas free from CO₂ and H₂O. Carburizing time: 5 hr. Rate of gas flow: 1 ft./min. x 100. (Reduced to four-fifths linear in reproduction.)

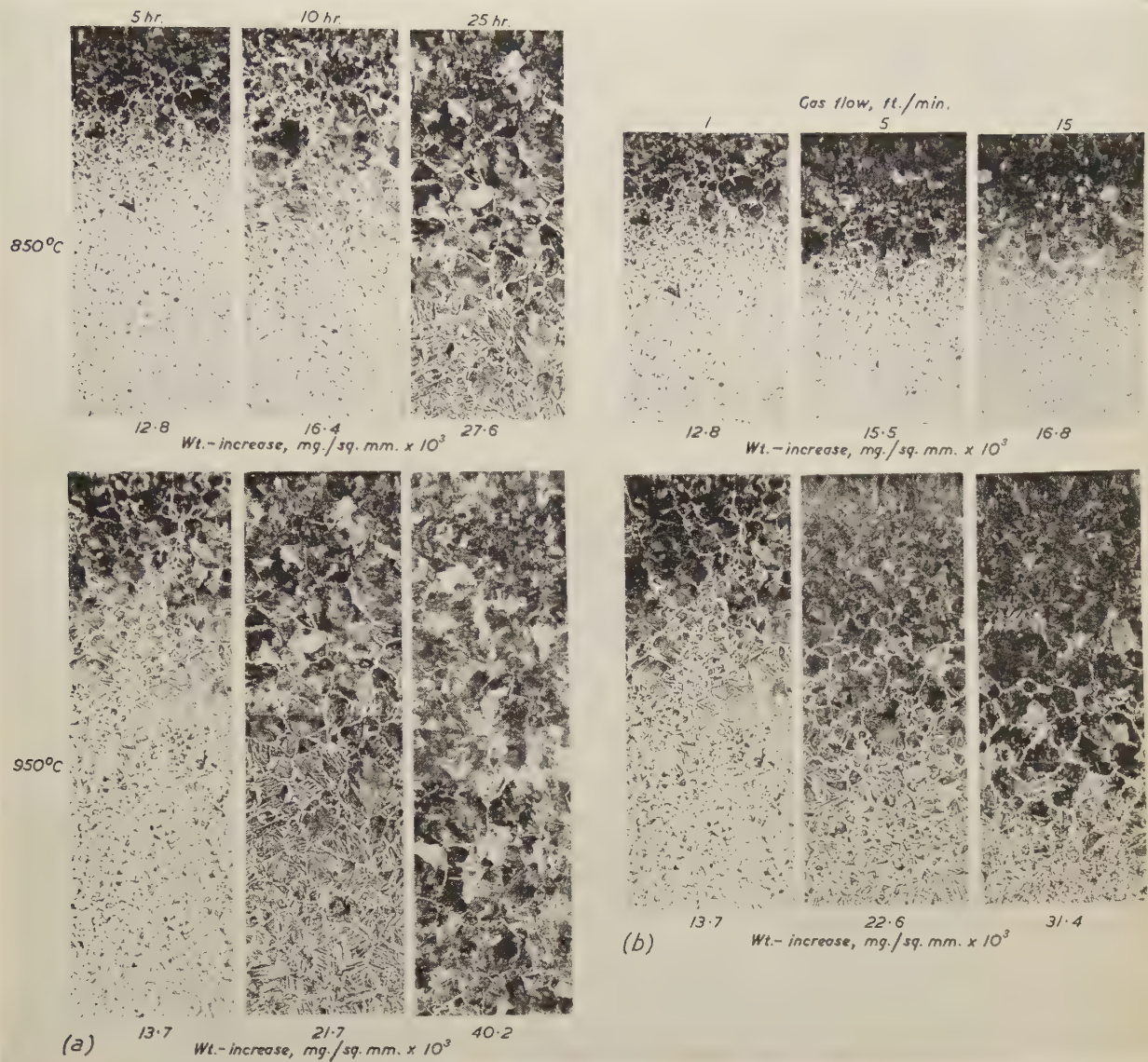


FIG. 15.—Mild Steel Carburized in Burnt Town's Gas free from CO_2 and H_2O . $\times 30$. Carburizing atmosphere: 10.7% CO , 15.0% H_2 , 74.3% N_2 . (a) Rate of gas flow: 1 ft./min., showing effect of carburizing time. (b) Carburizing time: 5 hr., showing effect of rate of gas flow. $\times 100$. (Reduced to one-half linear in reproduction.)

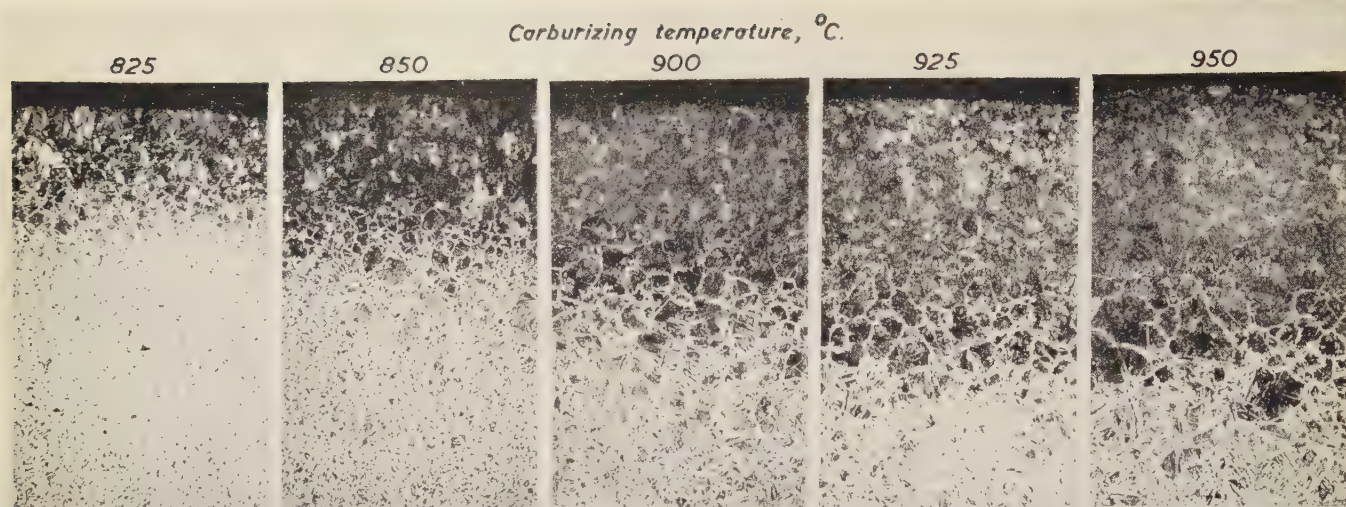


FIG. 16.—Effect of Carburizing Temperature on 0.15% Carbon Steel. Carburizing atmosphere: 21.3% CO, 1.3% H₂, 77.4% N₂. $\times 50$. (Reduced to two-thirds linear in reproduction.)

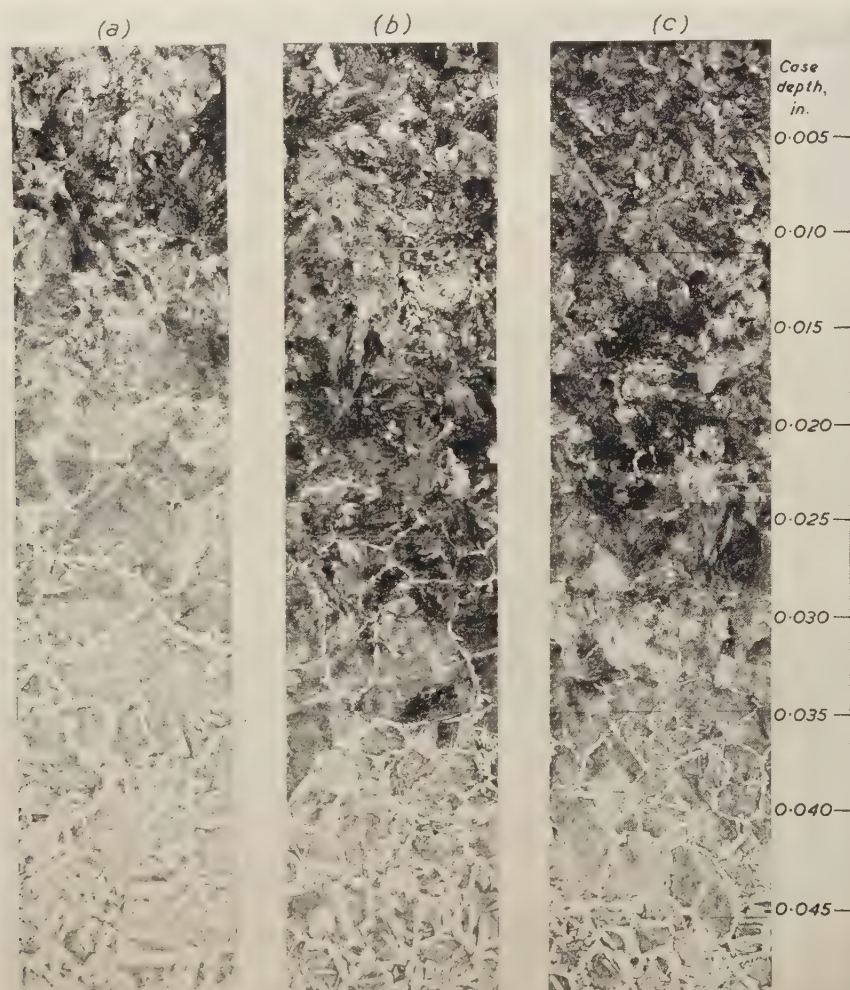
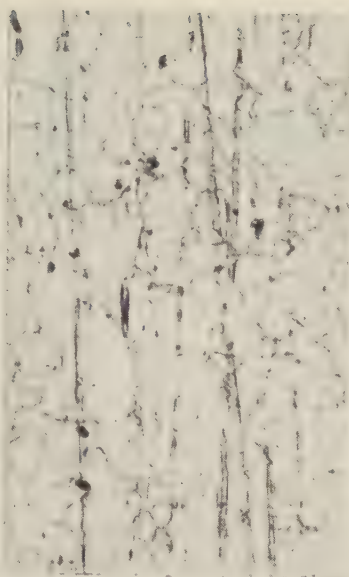


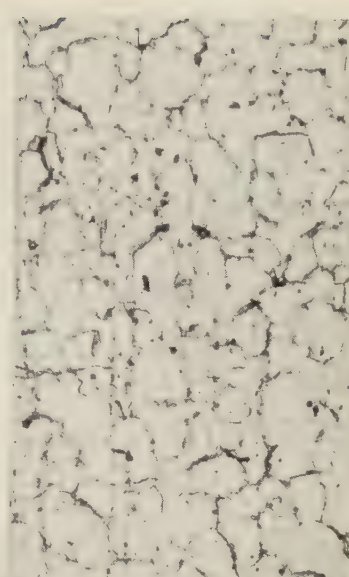
FIG. 17.—0.15% Carbon Steel Carburized at 925° C. for 5 hr. in Various Atmospheres. (a) "Reacted-gas" as generated: 24.5% CO, 35.5% H₂, 1.0% CH₄, 39.0% N₂, 0.1% H₂O. (b) "Reacted-gas" + 2% of Propane: 24.5% CO, 35.5% H₂, 1.0% CH₄, 39.0% N₂, 0.1% H₂O. (c) 4% Propane/96% Burnt town's gas pretreated over hot charcoal. $\times 200$. (Reduced to one-half linear in reproduction.)



As received



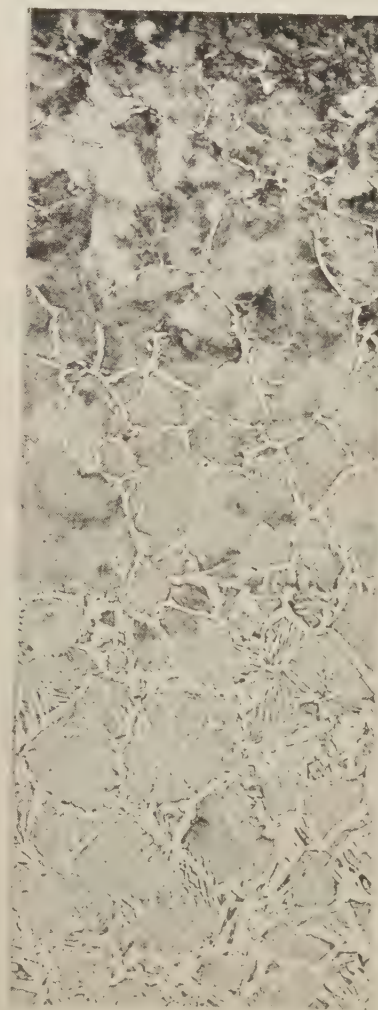
*After gas-etching
x 200*



*After etching and
carburizing*



*No etching
before
carburizing*



*Gas-etched
for 30 min.
before
carburizing.*

x 100

FIG. 18.—Effect of Gas Etching on the Degree of Carburization. Etching gas: 4.8% CO₂, 10.8% CO, 15.6% H₂, 2.3% H₂O, 66.5% N₂. Carburizing gas: 10.7% CO, 15.0% H₂, 74.3% N₂. Etching treatment: 30 min. at 950° C. Carburizing treatment: 5 hr. at 950° C.

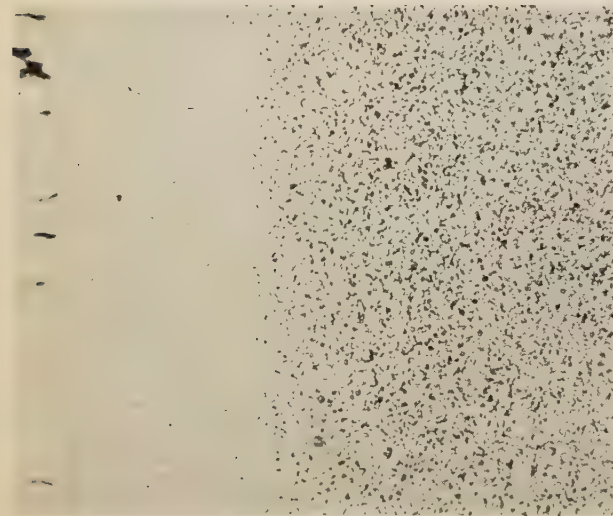


FIG. 19.—0.98% Carbon Steel. 20 hr. at 720° C.

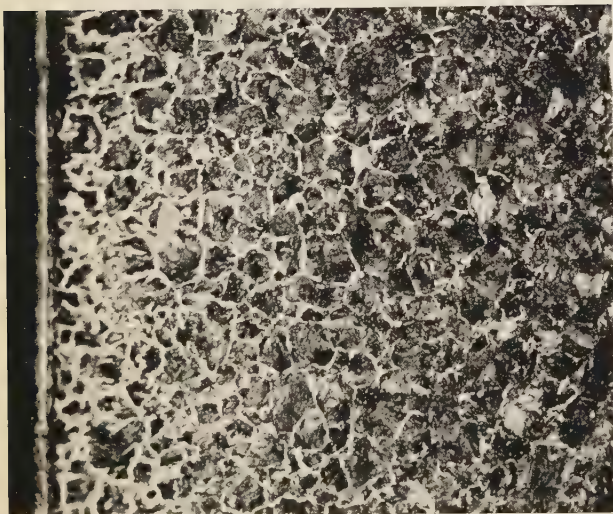


FIG. 20.—0.98% Carbon Steel. 20 hr. at 800° C.

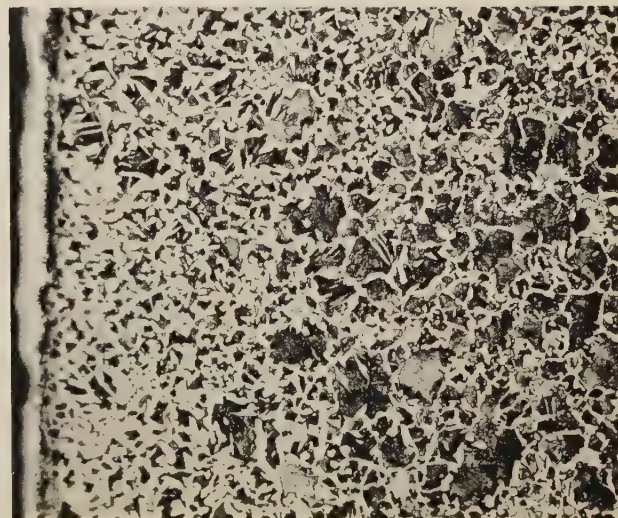


FIG. 21.—0.60% Carbon Steel. 20 hr. at 800° C.

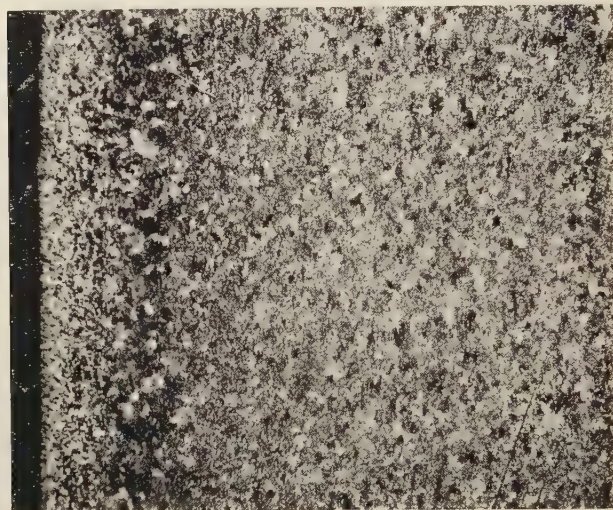


FIG. 22.—1.2% Carbon Steel. 6 hr. at 800° C.

FIGS. 19-22.—Decarburization of Carbon Steels in Charcoal. $\times 75$.



FIG. 23.—Case-Hardened Mild Steel, showing cracks at hyperitectoid case/core boundary. Picrate etch. $\times 75$. (Reduced to three-fifths linear in reproduction.)

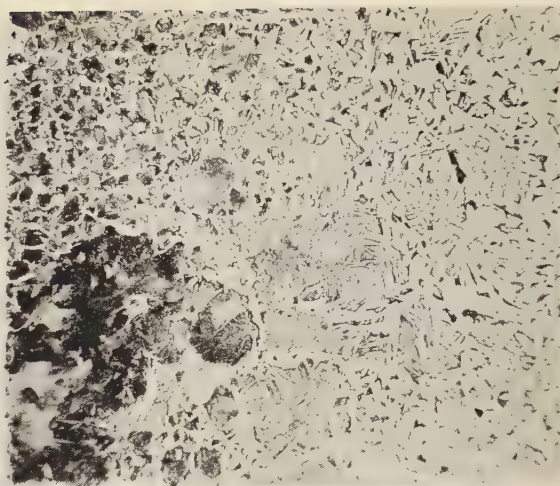


FIG. 24.—0.15% Carbon Steel Carburized at 875° C. (Ac₃). $\times 100$. (Reduced to four-fifths linear in reproduction.)

temperatures at which no sooting is obtained when the gas mixture does not reach the steel surface immediately on entry. Thus, in commercial installations, the use of forced circulation inside the carburizing container would promote the heating of the freshly charged gas before it meets the hot steel surface, and would tend towards a reduction in the amount of soot deposited on the work.

On the basis of the above results, experiments were carried out with the object of carburizing without carbon deposition the two alloy steels and the mild steel used in earlier work, in atmospheres of propane diluted with burnt town's gas preheated over charcoal. The alloy steels were treated at 900° C. and the mild steel at 925° C. for periods up to 10 hr. using the carburizing furnace illustrated in Fig. 5(b). Results are given in Table VIII., and some typical photomicrographs are shown in Figs. 9(c) and 10(c). It will be noted that by comparison with the carburizing atmospheres described previously, the charcoal-treated gas-propane mixtures employed resulted in improved penetration and gave higher concentrations of carbon in the surface layers. Carburization of the mild steel resulted in the formation of a hypereutectoid surface in all the atmospheres studied, even after only 2½ hours' treatment. Carburization of the nickel and nickel-chromium steels to hypereutectoid cases is indicative of the strongly carburizing nature of this type of atmosphere, and the surface-carbon analyses indicate that complete saturation of the austenite at the surface was obtained.

At very low concentrations of propane, increasing the hydrogen content of the diluting gas tended to reduce the extent of carburization somewhat, although this aspect of the matter calls for further investigation. The maximum carbon content of the case and the case depth were readily controlled by the concentration of propane added to the carrier gas.

All the mild-steel specimens treated in atmospheres containing 4% or less of propane were free from sooting, and were bright after treatment, although slightly etched and rather duller than in the as-received condition. Both the nickel and the nickel-chromium steels, under the conditions of test, were slightly sooted after carburization in atmospheres containing more than 2 and 1½% of propane respectively. Where sooting did take place it took the form, in the majority of tests, of merely a loose surface film which could be removed readily by brushing, leaving a clean, mat underlying surface. With forced circulation instead of streamlined flow, which was the condition obtaining in all the tests, it is very probable that higher concentrations of propane could be tolerated at the temperatures used in the experiments, without sooting resulting.

VI.—CARBURIZATION WITH CARBON-MONOXIDE-HYDROGEN ATMOSPHERES.

Bramley and his co-workers⁷ have studied the carburization of low-carbon steel in carbon monoxide, with and without the addition of certain hydrocarbon vapours, and have shown that, except at very high gas velocities, the extent of carburization compares very unfavourably with box-carburizing practice. It is probable that at gas velocities higher than those used by Bramley, greater concentrations of carbon would be obtained at the surface of the steel, but his results indicated that increasing the rate of gas flow had little effect upon the depth of case. Carburization in pure carbon monoxide therefore tends to produce shallow cases. Apart from this, however, as a commercial proposition, the use of pure or carburetted carbon monoxide is not an attractive proposition, mainly because of the difficulty in obtaining supplies of the gas in sufficient quantity and because of its high toxicity.

The comparative inactivity of pure carbon monoxide as a carburizing agent is in part due to the fact that at higher temperatures the gas becomes increasingly stable (see Fig. 3), the amount available for dissociation, and therefore for carburizing, being very small. As the temperature is raised and the equilibrium conditions for the carburizing reaction call for an ever-decreasing concentration of carbon dioxide, so it becomes necessary to increase considerably the velocity of the gas over the surface of the steel if a high surface concentration of carbon is to be obtained.

As has already been shown, preliminary investigations into the mechanism of carburization by the pack method indicated that the atmosphere in contact with the work was very rich in hydrogen and carbon monoxide, and it is suggested that the basic carburizing reactions are associated with either the desorption of carbon dioxide by hydrogen or the cyclic formation and decomposition of hydrocarbons, involving the carbon monoxide and hydrogen constituents of the atmosphere inside the box. Bramley⁷ has shown that the addition of hydrogen to pure carbon monoxide increases appreciably the potential carburizing power of the latter gas, the maximum rate of carburization being obtained with a carbon-monoxide/hydrogen ratio of 1 : 1.5. Carbon monoxide and hydrogen are major constituents of the type of controlled atmospheres produced by the combustion of fuel gases or of charcoal with air. Recent developments in this field have made it possible to produce, economically, atmospheres of this type from which decarburizing gases, such as carbon dioxide and water vapour, are readily removed. A study has been made of the carburizing properties of such atmospheres and the results obtained are discussed below.

Carburization in Purified Burnt Town's Gas.

Partly burnt town's gas contains carbon dioxide, carbon monoxide, hydrogen, water vapour, nitrogen, and possibly methane, in concentrations determined by the degree of combustion of the original raw gas. Industrial plants are available in which the carbon dioxide is removed by absorption in an organic solvent capable of regeneration, whilst water vapour is absorbed by, for example, activated alumina. For the purpose of the experiments, partly burnt town's gas as delivered by a standard commercial generator was freed completely from carbon dioxide by bubbling through a 25% solution of monoethanolamine in water, and then dried over activated alumina. The gas finally passed through a liquid-air trap. In certain experiments, water vapour in controlled amounts was re-introduced into the dried gas by bubbling it through a sulphuric acid solution of known strength, maintained at a constant temperature in a thermostatically controlled water-bath. Vapour-pressure data from the International Critical Tables were used for calculating the percentage of water vapour introduced. Carburization of mild steel in the atmosphere processed in this way was carried out in the apparatus shown in Fig. 5(a). Photomicrographs of the treated specimens are shown in Figs. 14 and 15(a), and other results are given in Figs. 25 and 26.

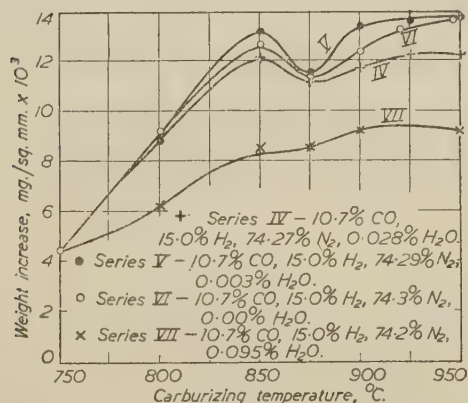


FIG. 25.—0.15% Carbon Steel Carburized in Various Burnt-Town's-Gas Atmospheres. Carburizing time: 5 hr. Gas flow: 5 litres/hr. (1.0 ft./min.).

For a given gas composition the rate of carburization increased with temperature, but below the upper critical point of approximately 875° C. the case was very shallow, with a steep gradient from the surface to the core. This was found to be independent of the composition of the gas used and is probably associated with the low rate of diffusion of carbon in the austenite-ferrite complex.

This rate of carburization increased with the carbon monoxide content of the atmosphere, but a water-vapour content above 0.003% was found

to reduce the carburizing power of the gas quite considerably, whereas below this concentration the rate of carburization was found to be greater than that obtained with the perfectly dry gas. It is probable that small traces of water vapour activate the steel surface by cyclic adsorption-desorption reactions, without being present in sufficient concentration to promote decarburization. At gas velocities of the order of 15 linear ft./min. the degree of carburization approached a constant value (Figs. 15(b) and 26). At 950° C.

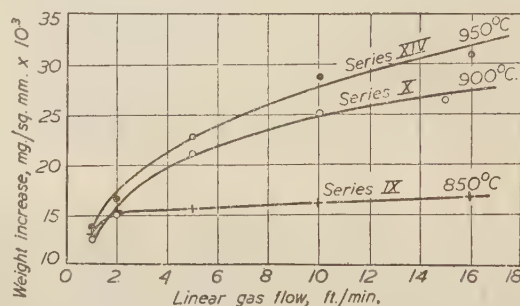


FIG. 26.—0.15% Carbon Steel Carburized in a Diluted CO-H₂ Atmosphere, showing effect of gas flow on carbon absorption at various temperatures. Carburizing gas: 10.7% CO, 15.0% H₂, 74.3% N₂. Carburizing time: 5 hr. Surface of specimen abraded with No. 0 emery cloth before test.

the maximum rate of carburization obtained under optimum conditions of atmosphere composition and rate of flow was approximately 0.010 in./hr. for treatments up to 5 hr. in duration, giving a surface hardness on the steel quenched from 825° C. of 870 diamond pyramid number.

Carburization in Burnt Town's Gas Pretreated over Charcoal.

As previously mentioned, carbon dioxide and water vapour can be eliminated from burnt town's gas by passing the mixture over charcoal heated to approximately 1000° C. (see Table VII.). Reactions between the carbon and the decarburizing gases result in an increase in both the carbon monoxide and hydrogen contents of the burnt town's gas, according to reactions (1) and (4).

Carburization of mild steel at temperatures ranging from 825° to 950° C. in an atmosphere produced as above was carried out in the carburizing furnace shown in Fig. 5(b). Results of the tests are given in Fig. 27 and Table IX., and photomicrographs of the types of case produced are shown in Fig. 16. An atmosphere of this type is much more strongly carburizing, under comparable conditions of test, than is the atmosphere produced by the chemical purification of burnt town's gas, a rate of carburization being obtained which is comparable with that reached in box-carburizing practice. It is interesting to note from Fig. 27 that the concentration of carbon in

the surface of the steel is far greater at temperatures below the upper critical change point than above it. It is probable that this is associated with the formation of a surface film of pure cementite, possibly only a few molecules thick. Owing to the slow rate of diffusion of carbon in the austenite-ferrite phase, there is a greater

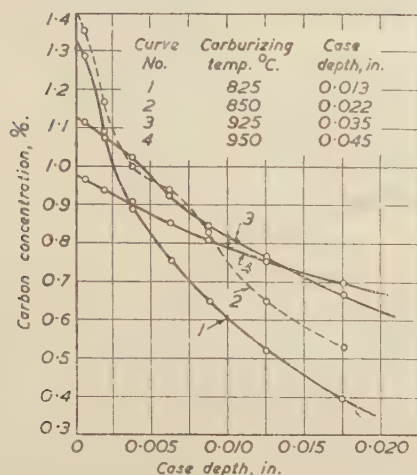


Fig. 27.—0.15% Carbon Steel Carburized in Carbon Monoxide. Carburizing gas: 21.3% CO, 1.3% H₂, 77.4% N₂. Carburizing time: 5 hr.

tendency for the concentration of carbon to build up at the steel surface, and a correspondingly greater opportunity for the formation of a surface film of cementite. In the pure austenitic phase, the rates of absorption and diffusion of carbon are so markedly increased that there is little opportunity for the formation of a continuous surface film of iron carbide.

As in the case of the chemically purified burnt

town's gas, mild-steel specimens carburized at temperatures above 800° C. in burnt town's gas pre-heated over charcoal, remained perfectly bright throughout the treatment. Specimens treated below 800° C., however, possessed a very light but adherent surface film of carbon after treatment. This phenomenon is of particular significance and is discussed later in greater detail.

Carburization in Reacted Town's Gas.

The partly burnt town's gas normally used for bright-annealing is obtained by the combustion of town's gas with air in a volume ratio which is always within the limits of combustibility, and the heat of combustion is utilized to maintain the temperature of the combustion chamber of the generator within a recommended range. However, a fuel-gas/air mixture can be so rich in gas as to be virtually non-combustible, but if such a mixture is heated, then reactions between the gases take place in which the free oxygen is consumed, the hydrocarbons are converted to carbon oxides and hydrogen, and the general trend is towards the establishment of a high-temperature equilibrium with the minimum possible number of active gases. The whole process is endothermic, and is promoted at high temperatures by metal catalysts or by charcoal. Provided that the temperature is sufficiently high, an atmosphere can be produced free from carbon dioxide and having a very low dew-point.

A typical composition of an atmosphere generated in this way is as follows:

Carbon Monoxide.	Methane.	Hydrogen.	Nitrogen.	Water Vapour.
24.4%	1.0%	35.6%	39.0%	0.1%

The above atmosphere, produced from a ratio of

TABLE IX.—Carburization of 0.15% Carbon Steel in Various Atmospheres.

Carburization: 5 hr. at 925° C. Rate of gas flow: 5 linear ft./min.

Carburizing Atmosphere.	Composition of Carburizing Atmosphere.									Weight Increase, mg./sq. mm. × 10 ³ .	Surface Carbon Content, %.	Case Depth, in.	Appearance of Carburized Work.
	CO ₂ , %.	C ₂ H ₆ , %.	CO, %.	H ₂ , %.	CH ₄ , %.	H ₂ O, %.	N ₂ , %.	O ₂ , %.	C ₂ H ₂ , %.				
Raw town's gas	2.6	2.4	11.0	56.0	21.5	2.0	4.5	37.5	0.80	0.037	Heavily sooted.
Purified town's gas	9.0	52.5	20.1	...	18.5	56.0	1.20	0.060	Lightly sooted.
32% Propane, 68% air	53.5	14.5	32.0	50.5	1.10	0.055	Heavily sooted.
32% Propane, 68% burnt town's gas	3.3	...	7.4	10.6	...	1.6	45.0	...	32.0	50.5	1.20	0.062	Heavily sooted.
6% Propane, 94% purified burnt town's gas	19.6	1.1	73.3	...	6.0	58.1	1.24	0.066	Clean, mat.
Chemically purified burnt town's gas	10.7	15.0	74.3	22.0	0.88	0.032	Clean, bright.
Charcoal-treated burnt town's gas	21.3	1.2	77.5	47.0	1.13	0.035	Clean, mat.
Reacted town's gas	24.4	35.6	1.0	0.1	39.0	45.0	1.00	0.040	Clean, mat.
98% Reacted gas, 2% propane	23.8	34.8	1.0	0.1	38.3	...	2.0	50.2	1.16	0.058	Clean, mat.
Steam-charcoal gas	49.0	48.5	2.5	48.8	1.03	0.050	Clean, mat.

air to town-gas of $1\frac{1}{4}:1$, has been used for carburization experiments. The type of case produced on a 0.15% carbon steel after carburizing at 925° C. for 5 hr. is shown in Fig. 17(a). Additional experiments were carried out with the same atmosphere to which was added 2% of propane. As will be seen from Fig. 17(b), the small trace of water vapour has quite a marked effect in reducing the carburizing power of the gas, but this can be counteracted either by drying the gas over activated alumina or by the addition of a low concentration of propane. Alternatively, generation of the atmosphere at a higher temperature will reduce even further the concentration of water vapour.

The surface carbon content obtained in the non-carburetted atmosphere was only just above the eutectoid composition. The addition of 2% of propane resulted in an increase in the surface carbon content to a value corresponding to almost complete saturation of the austenite at 925° C. and resulted in addition in a considerably improved depth of case. The atmosphere gives bright carburization when not carburetted and is explosive when mixed with air.

Carburization in Gas Generated from Steam and Charcoal.

It has already been shown that the atmosphere generated inside a carburizing box is probably in the main associated with the reaction of absorbed water vapour and the charcoal. Experiments have been carried out, therefore, to investigate the carburization of carbon and alloy steels in an atmosphere produced by the reaction of steam on hot charcoal. Because of the endothermic nature of the reaction involved, the atmosphere generator consisted of a retort, heated externally by means of an electric furnace to approximately 1000° C. The atmosphere generated under these conditions had the following composition :

Carbon Monoxide.	Hydrogen.	Methane.	Water Vapour.
49.0%	48.5%	2.5%	0.1%

Carburization of the 0.15% carbon steel at 925° C. and a nickel-chromium-molybdenum case-hardening steel at 900° C. has been carried out in this atmosphere, completely dried over activated alumina. Fig. 28 shows the case depths obtained by the carburization of the alloy steel in a cyanide bath, in a 28% propane/72% air mixture, and in the steam-charcoal atmosphere as generated. The amounts of carburization produced in the two gas mixtures compare very favourably with each other, that in the steam-charcoal gas giving a rather steeper initial carbon gradient than that in the air-propane mixture. On the other hand, carburization in steam-charcoal gas gives a clean, soot-free surface, and this results in a much more uniformly carburized case.

The rich hydrocarbon atmosphere leads to a hypereutectoid type of case, frequently having quite a deep zone of cementitic network. On the whole this is not desirable, since on hardening exfoliation of the case can result (Fig. 23), and it is advisable to follow such a carburizing treatment with a diffusion period in which the surface carbon content is reduced to the eutectoid composition. The carbon-monoxide/hydrogen atmo-

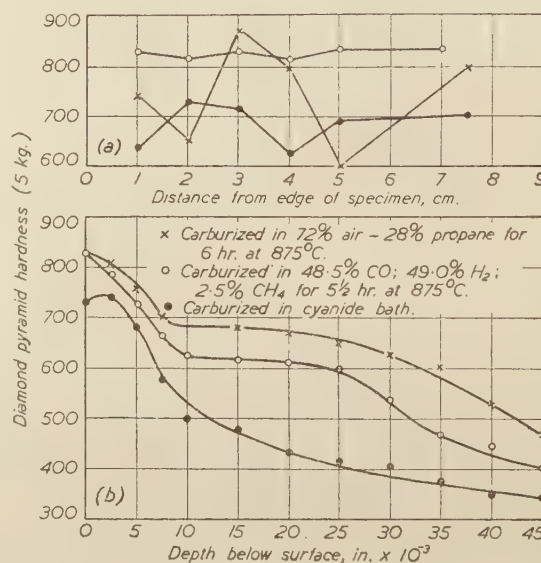


FIG. 28.—Hardness of Carburized Nickel-Chromium-Molybdenum Steel. All samples O.H. from 775° C. (a) Hardness along surface, (b) hardness below surface.

sphere, however, produces a case with a maximum carbon content only slightly above the eutectoid composition, the depth of the case on the whole being slightly less than that obtained in the diluted hydrocarbon type of atmosphere. On the other hand, the production of this type of case, with which there is no need for a diffusion period, may be, on the whole, the more satisfactory.

VII.—THE NATURE OF THE STEEL SURFACE AND ITS EFFECT UPON THE RATE OF CARBURIZATION.

The rate of carburization in any atmosphere can be influenced considerably by the condition of the steel surface; this aspect of the subject has been investigated, using a carburizing gas of burnt town's gas from which the carbon dioxide and water vapour had been completely removed. Flat mild-steel specimens were used for the experiments, carburization being carried out in all cases at 950° C. for 5 hr. The surfaces were mechanically roughened by sand- or shot-blasting or by abrasion on emery cloth. Mat surfaces were produced by oxidizing the steel in air at 950° C. before carburization. Results typical of those obtained are given in Table X. Mechanical

TABLE X.—*Effect of Surface Condition of 0.15% Carbon Steel on the Degree of Carburization in Dry-CO₂/Free-Burnt-Town's-Gas.*

Carburizing temperature : 950° C. Carburizing time : 5 hr.

Gas Flow, ft./min.	Surface of Specimen.	Carburizing Atmosphere.	Weight Increase, mg./sq. mm. × 10 ³ .
1	Abraded with No. 0 emery cloth.	10.7% CO, 15% H ₂ , 74.3% N ₂ .	13.9
1	Sand-blasted.	" " "	12.0
1	Shot-blasted.	" " "	12.1
1	Pre-oxidized for 10 min. at 950° C.	" " "	15.3
1	Oxidized for 1 min. at 1-hr. intervals during carburizing.	" " "	8.45
1	Pre-oxidized; oxidized again for ¼ min. after 2½ hours' carburization.	" " "	13.10
5	Abraded with No. 0 emery cloth.		21.60
5	" " "	0.05% O ₂ , } 10.7% CO, 15% H ₂ ,	18.20
5	" " "	0.10% O ₂ , } remainder N ₂ .	13.70

roughening or pickling of the surface had little effect on the rate of carburization, as indicated by the weight of carbon absorbed per unit area. An oxidized and reduced surface was rather more receptive to carbon absorption than was a bright cold-rolled surface, but the order of the increase obtained is insufficient to justify the introduction of an additional process before carburization.

A burnt fuel gas can progressively roughen a bright steel surface if chemical equilibria for the so-called "producer-gas" and "water-gas" reactions are not satisfied at the temperature of treatment :



The reactions proceed to equilibrium at the high temperature, catalysed by the steel surface, which becomes etched and very active, chemically, in the process. It is probable that during the etching treatment some decarburization of the steel takes place by both the carbon dioxide and the water vapour present in the burnt town's gas, and in this connection it is interesting to note that in the carburization of armour plate, it is sometimes the practice to give the material a short decarburization treatment before carburizing, since this is found to improve the rate of carburization.

Experiments have been carried out to determine the effect of a gas-etching treatment upon the rate of carburization of a low-carbon steel, carburized in purified burnt town's gas.¹³ The procedure was to heat the specimen to the carburizing temperature in the burnt-town's-gas atmosphere as supplied by the atmosphere generator. This gas contained, in addition to carbon monoxide, hydrogen, and nitrogen, the decarburizing gases carbon dioxide and water vapour. The atmosphere composition selected was one which was known to cause pronounced etching after only a short time of treatment at 950° C. The atmosphere used for etching was the basis of the

carburizing atmosphere, which was produced by the complete absorption of the carbon dioxide and the water vapour from the original burnt town's gas. Thus, after the etching period was completed, the carburizing gas was brought on to the furnace tube and carburization proceeded for the predetermined time of test. The results are given in Table XI. and are illustrated in Fig. 18. It will be noted that the rate of carburization was increased appreciably even after quite a short pre-etching time. The surface carbon content increased and the case depth was more than doubled after an etching time of only 30 min. Alternate etching and carburization did not give satisfactory results, since the etching atmosphere is very decarburizing and the loss of carbon during the intermediate etching treatments of a steel already carburized, more than offsets the increased rate of carburization resulting from the etching.

The greater rate of carburization appears to be associated with an increase in the chemical activity of the steel surface, and cannot be attributed to the lower initial carbon content of the surface of the steel after the etching treatment. The process of carburization itself activates a steel surface owing to progressive roughening, so that etching in a complex atmosphere such as is described above merely serves to prepare the surface for a rapid initial rate of carburization. Once the surface has become activated, continued carburization maintains the activity at the highest possible level. Contamination of the surface during carburization decreases this activity, however, and results in an overall decrease in the rate of carburization.

VIII.—THE EFFECT OF TEMPERATURE ON CARBURIZATION.

For carburization to proceed at a satisfactory rate it is necessary for the steel to be in a condition which readily absorbs the nascent carbon supplied to it at the surface. The foregoing ex-

TABLE XI.—*Effect of Gas-Etching upon the Degree of Carburization of Steel in an Atmosphere of Dry CO₂ and Free Burnt Town's Gas.*Analysis of burnt town's gas : 10.7% CO, 15.0% H₂, 74.3% N₂.

Steel.	Temp. of Etching and Carburization, ° C.	Gas Flow for Etching, ft./min.	Time of Etching, min.	Gas Flow for Carburization, ft./min.	Time of Carburization, hr.	Analysis of Atmosphere for Etching.	Weight Increase, mg./sq. mm. × 10 ³ .
0.15% C steel.	950	1	5	No etching.	13.90
	950	2	5	1	5	7.3% CO ₂ , 4.6% CO, 6.5% H ₂ , 2.3% H ₂ O, 79.3% N ₂ .	15.00
	950	2	15	1	5		16.40
	950	2	30	1	5		17.10
	950	2	5	1	5	4.8% CO ₂ , 10.8% CO, 15.6% H ₂ , 2.3% H ₂ O, 66.5% N ₂ .	16.65
	950	2	15	1	5		18.60
	950	2	30	1	5		19.90
3.17% Ni, 0.16% C case-hardening steel.	900	10	5	No etching.	16.10
	900	5	5	No etching.	12.60
	900	2	30	5	5	4.8% CO ₂ , 10.8% CO, 15.6% H ₂ , 2.3% H ₂ O, 66.5% N ₂ .	16.50

periments have shown that below the upper critical point for the steel, *i.e.*, in the ferrite-austenite phase, the rate of solution of carbon by the iron is comparatively slow. On the other hand, γ -iron dissolves carbon very readily, and the cementation process is invariably carried out above the upper critical point for the steel.

Steel can be carburized below the austenitic change point, but the slow rate of the reaction results in a sharply marked boundary between the carburized zone and the unchanged core. This is associated with the slow rate of solid diffusion of carbon from the surface to the core. The effect of temperature upon the rate of carburization was very markedly brought out in the experiments on the carburization of mild steel in an atmosphere of burnt town's gas, free from carbon dioxide, results of which are shown in Fig. 25. It will be noted that near to the upper critical point—which for the steel in question is 875° C.—there is a marked falling off in the extent of carburization as indicated by the increase in weight. A similar effect was obtained when the steel was carburized in a more strongly carburizing agent, such as a solid carburizer or a mixture of 3% propane/97% charcoal-treated-burnt-town's-gas (Fig. 29). Between 875° C. and the lower transformation point of 725° C., the steel consists of ferrite and austenite, the latter increasing in concentration up to 100% at the upper change point, *i.e.*, 875° C. At any temperature within this range the ferrite is saturated with carbon, whilst the austenite is of fixed carbon content, corresponding to that of a steel having an Ac₃ point at the temperature in question, and a state of equilibrium is set up between the ferritic and the austenitic phases. Absorption of the carbon at the surface can take place only *via* the austenitic

phase, which thereby becomes supersaturated with carbon with respect to the adjoining ferritic areas. The excess of carbon diffuses to the austenite-ferrite boundaries, where transformation takes place progressively with the conversion of ferrite

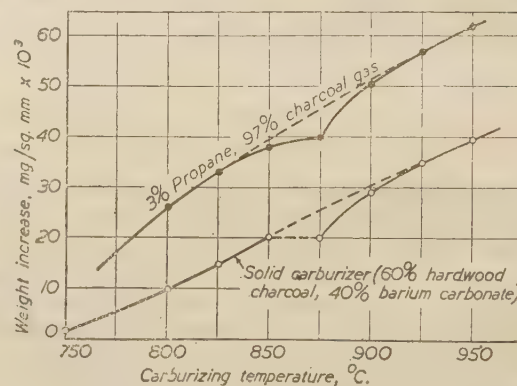


FIG. 29.—Effect of Temperature on Carburization. Values include slight surface deposits of soot.

to austenite. This rather complex mechanism probably accounts in some measure for the low rate of carburization in the austenite-ferrite range as compared with that in a simple austenitic structure. It does not, however, offer a ready explanation for the marked falling off in the carburization rate at temperatures on either side of the critical point of the steel.

Within the temperature range 725–875° C. the increasing rate of carburization with temperature shown in Figs. 25 and 29 is due both to the increased rate of diffusion of carbon in austenite and to the increased concentration of the latter phase present in the steel as the upper critical temperature is approached. At the same time, however,

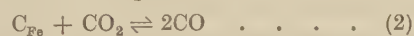
there is a progressive change taking place in the grain-size characteristics of the steel and the structure becomes more homogeneously fine-grained as the carburizing temperature is increased, the minimum homogeneous grain-size being reached at or very near to the Ac_3 point. Fine-grained steels do not carburize so rapidly or uniformly as coarse-grained steels, and it is suggested that the falling-off in the rate of carburization observed in the above experiments near to 875°C . is associated with the changes in the grain-size characteristics of the steel during the transformation from the austenite-ferritic complex to the wholly austenitic state. This view is supported by the fact that at or near to the Ac_3 point of a steel, carburization can be very non-homogeneous, as shown in Fig. 24, and is comparable with the development of so-called abnormal structures in carburized steels of inherent small grain-size.

When carburization is carried out below the upper critical temperature for the steel, there is at any time a zone within the cemented case in which the carbon content is equal to that of a steel having an Ac_3 point at the particular carburizing temperature. This zone is fine-grained (see Figs. 14, 15, and 16), and it is suggested that it serves as a partial barrier between the core and the outer zones of the case, slowing up the rate of carburization and promoting a sharply marked carbon gradient between the case and the core.

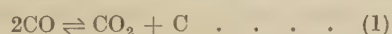
In view of the above observations it is important that a carburization temperature should be selected which is $25\text{--}50^\circ\text{C}$. above the Ac_3 point for the steel, but is below its grain-coarsening temperature.

IX.—THE RELATIVE ACTIVITIES OF SOLID CARBON AND CEMENTITE.

When a carbon steel is treated at a suitable high temperature in an atmosphere containing carbon dioxide, direct reaction may take place between this gas and the carbon in the steel according to the following reaction :



If the carbon monoxide is in excess of that required for equilibrium in this reaction, the steel is carburized. Under certain conditions, however, it is also possible for the carbon monoxide to deposit on the steel surface free carbon which does not enter into solution in the iron :



The equilibrium constants K for these two reactions are represented by the following ratios :

$$K_1 = \frac{(CO)^2}{(CO_2) \times (C_1)} \quad . \quad . \quad . \quad (1a)$$

$$K_2 = \frac{(CO)^2}{(CO_2) \times (C_2)} \quad . \quad . \quad . \quad (2a)$$

where the factors C_1 and C_2 represent the activity of carbon in the gas phase over solid carbon and over iron saturated with carbon respectively. The activity of carbon in solution in the steel varies with the concentration of carbon, being at a maximum at a given temperature when the steel is fully saturated. Whilst the equilibrium constants K_1 and K_2 are identical at any given temperature, the ratios of carbon monoxide to carbon dioxide for the two reactions differ, that for reaction (5) being determined by the concentration of carbon in the surface of the steel. Equilibrium curves for various carbon steels, according to Becker,¹⁰ are shown in Fig. 30.

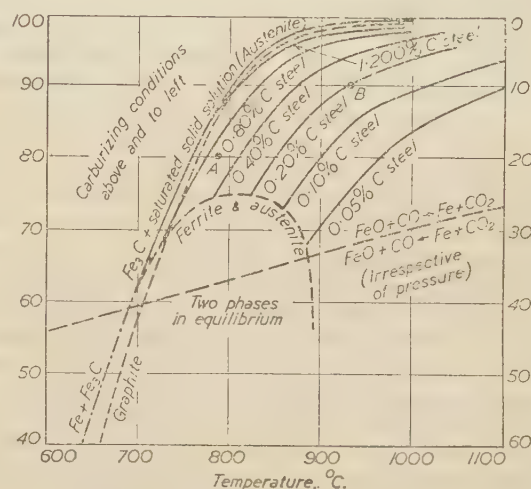


Fig. 30.—Equilibrium for the System $CO-CO_2-Fe-C_{Fe}$ (Becker). Carburizing curves are for 1 atmosphere pressure.

The relationship between the activities of solid carbon (C_1) and of carbon in a saturated solution in the steel (C_2) is of some importance in that it determines which of the two reactions (1) and (2) predominates at the temperature of treatment. If C_2 is less than C_1 , i.e., if cementite is stable with respect to solid carbon, from a consideration of the equilibrium ratios for the respective reactions it will be seen that at any temperature the concentration of the carbon monoxide necessary for equilibrium is less with respect to cementite than it is with respect to solid carbon. Consequently, if the atmosphere used satisfies equilibrium conditions for reaction (1) at temperatures above approximately 725°C ., some carburization of the steel takes place. On the other hand, if the reverse is the case and it is the solid carbon which is stable with respect to the cementite, then the atmosphere in equilibrium with the latter is richer in carbon monoxide than that in equilibrium with solid carbon at the same temperature. In such a case an atmosphere which is balanced with respect to cementite in the steel contains excess of carbon monoxide with respect

to equilibrium with solid carbon, and sooting may result from the progress of the producer-gas reaction (1) to equilibrium. If the atmosphere is balanced with respect to reaction (1), however, decarburization of the steel will take place. An atmosphere having a composition intermediate between the two sets of equilibrium concentrations can therefore lead to both sooting and carburization.

Johansson and his co-workers¹⁵ have studied the relationship between the respective activities of graphite and of austenite plus cementite and have reported that below 800° C. graphite is stable with respect to cementite, but that above this temperature there is a reversal. Becker,¹⁰ on the other hand, has reported that within the temperature range 650–1000° C. the activities of cementite is higher than that of graphite and hence that over this temperature range graphite is always stable with respect to iron carbide. With increasing temperature, however, the carbon content of the saturated austenite solid solution, having a carbon activity equal to that of graphite, also progressively increases. Thus at 750° C. the carbon content of the austenite having a carbon activity equivalent to that of graphite is approximately 0.6%; at 800° C., 1%; and at 900° C., approximately 1.2% (Fig. 30). Thus, low-carbon steel heated in charcoal is carburized to a surface carbon content of 1% at 800° C. and 1.2% at 900° C. Bramley and Lord¹⁶ in their work on the gaseous carburization of iron have supported the conclusions of Becker with regard to the relationship between the respective activities of graphite and cementite, although the actual values obtained for the ratio of the respective activities at various temperatures are not concordant.

The foregoing work on the gaseous cementation of steel in various carburizing atmospheres has thrown some light on the relationship between the respective activities of solid carbon, and of cementite in a saturated solution of austenite. In atmospheres of the non-carburetted type, containing simply carbon monoxide, hydrogen, and nitrogen, carburization of low-carbon steel at temperatures above 800° C. could be obtained readily without any surface discoloration of the work. In every case, however, when such atmospheres were used for carburization below 800° C. carburization was accompanied by light sooting. This was independent of the concentration of carbon monoxide above its equilibrium concentration with respect to carbon dioxide for reaction (2), and of the time of treatment. These results indicated that below 800° C. the soot was stable with respect to cementite. X-ray examination showed that the soot was amorphous carbon.

That amorphous carbon is the stable phase at temperatures below 800° C. is further borne out by the fact that high-carbon steel when heated in

charcoal at temperatures below 800° C. is decarburized (Figs. 19–22). At temperatures above 800° C. however, carburization of low-carbon steel in charcoal is readily obtained and high-carbon steel can be heated under such conditions without decarburization taking place.

No attempt has been made to determine the actual values of the activities of cementite and the various forms of solid carbon. The difference in the values at any temperature must be very small indeed and must call for great accuracy in its determination. The sole purpose of this brief discussion of the subject has been to bring out the fact that observations during the work on gaseous-cementation processes indicate that the view that below 800° C. solid carbon is stable with respect to cementite, and that above this temperature the reverse is the case, applies only to amorphous but not to graphitic carbon.

X.—SUMMARY AND CONCLUSIONS.

(1) Analyses of samples of gas extracted from a carburizing box at the temperature of carburization have shown that hydrogen, as well as carbon monoxide, is a major constituent of the atmosphere surrounding the work. It is considered that the main source of the atmosphere in the box is the reaction between the hot carbon and water vapour absorbed in the capillary pores of the charcoal of the carburizing compound.

(2) The mechanism whereby carbon is transferred from the carburizing medium to the steel has been discussed with respect to box- and gas-carburizing processes. It is considered that the hydrogen formed in high concentrations in a carburizing box plays an active part in the process either by desorption of carbon dioxide or by reacting with the charcoal to form hydrocarbon gases. The cyclic formation and decomposition of the latter supplies the nascent carbon to the steel. In the case of gas-carburization processes, the carbon is supplied either from a gas such as propane, which is thermally unstable at the carburizing temperature, or from one such as methane or carbon monoxide, which is present at the carburizing temperature in excess of its equilibrium concentration with respect to fully saturated austenite.

(3) The carburizing properties of raw hydrocarbon gases such as town's gas and butane have been investigated. The ready deposition of soot from both gases interferes with the carburization reaction and in extreme cases can completely inhibit carburization. Town's gas contains decarburizing gases which offset to a large extent the carburizing constituents. The processing of town's gas in order to eliminate the unsaturated hydrocarbons and the decarburizing gases results in an atmosphere being obtained which is strongly

carburizing, although the tendency to sooting is not completely eliminated.

(4) The carburization of three commercial case-hardening steels in diluted propane atmospheres has been studied. Diluting agents such as air and burnt town's gas call for high concentrations of propane to offset the decarburizing gases present. To obtain anything approaching a maximum rate of carburization, propane contents above 25% have to be considered, with the result that the tendency to sooting is considerably increased. It has not been found possible, when using either air or burnt town's gas as a diluting agent, to eliminate sooting and still to maintain the maximum carburizing rate.

(5) A diluting agent which contains no decarburizing gases can be generated by the treatment of burnt town's gas over charcoal at approximately 1000° C. Carbon dioxide and water vapour can be completely removed by reactions with the charcoal and the resulting gas is itself carburizing. Concentrations of propane of the order of only about 2% are sufficient to make the atmosphere very strongly carburizing, and because of the low concentration of the hydrocarbon gas a maximum rate of carburization without sooting can be obtained.

(6) The carburizing properties of carbon-monoxide/hydrogen atmospheres, prepared from town's gas, charcoal, or both, have also been investigated. The atmosphere generated by the treatment of rich town's-gas/air mixtures over charcoal, maintained at a temperature sufficiently high to eliminate carbon dioxide and water vapour, has excellent carburizing properties. The addition of a small concentration of propane safeguards against any trace of decarburizing gas that may remain in the generated atmosphere, and results in a maximum rate of carburization without sooting. As distinct from the diluted propane atmosphere, which tends to produce a hyper-eutectoid case with a deep cementitic network, the carbon-monoxide/hydrogen type of atmosphere produces a surface near to the eutectoid composition, with a case of rather less depth. However, the need for a diffusion period to remove the cementitic network is avoided.

(7) Experiments with carbon-monoxide/hydrogen atmospheres have tended to confirm the view that these two gases can be strongly carburizing even in the absence of solid carbon.

(8) The effect of the steel surface upon the rate of absorption of carbon by a steel has been investigated. Roughening the surface by heating the steel in an atmosphere in which inter-gas

reactions are promoted by the steel, markedly increases the activity of the surface and speeds up the rate of carburization.

(9) The temperature of carburization and its effect on the rate of carburization is also discussed, and it is shown that at and just below the upper critical point of the steel being treated, the rate of absorption of carbon falls off markedly. It is suggested that this is associated with grain refinement during heating up to the Ac_3 part, which in turn promotes a sharp gradient between the case and the core.

(10) The relative activities of solid carbon and of cementite have been discussed and it is concluded, from observations made in the course of the foregoing investigations, that below about 800° C. solid amorphous carbon is stable with respect to cementite, but that above this temperature the reverse is the case.

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CORRESPONDENCE.

Mr. F. R. MORRAL (American Cyanamid Company, Stamford, Conn., U.S.A.) wrote: This paper has been of interest to us. However, the paragraph on the second page devoted to liquid carburizing is believed to be somewhat misleading. There are three types of liquid-carburizing baths used commercially. All of these have been extensively used in the United States during the war period. Liquid carburizing, which is a relative newcomer, permits obtaining hypereutectoid cases and case depths to 0.150 in. by using the proper bath times and temperatures, and is successfully competing with gas- and pack-carburizing.

Mr. C. C. HODGSON (Leyland Motors, Ltd., Lancashire) wrote: The paper by Mr. Ivor Jenkins is a valuable contribution to the literature on carburizing. It would have been of still greater value had it included particulars of more gas-carburizing runs on carbon case-hardening steel at a temperature of 900° C.; as the paper stands at present it is difficult to make a direct comparison between the results obtained from the three steels; there seem, however, to be certain anomalies.

The case depth of the 3% nickel steel is always shown as considerably less than that of nickel-chromium steel and the gain in weight of the latter is always the greater. This trend is in agreement with the generally accepted views, but Mr. Jenkins' figures often seem to show inconsistencies. For example, in Table IV., the six sets of results at the beginning of this Table are stated in the text to have been obtained from specimens that were not seriously "sooted," but we are asked to believe that the rate of penetration of carbon in the nickel-chromium steel is from (approximately) 50 to 180% faster than it is in the nickel steel. Now, as every observant practical case-hardener knows, this is not true, at least in pack-hardening practice. The diffusion rate in 3% nickel steel when using solid carburizer is at least 85% of that of a 3% nickel-chromium steel at the same temperature (900° C.).

These differences may in part be due to the method of measuring the case depth used by Mr. Jenkins; measuring the case depth at the place where the carbon content is estimated to be of the order of 0.3–0.4% may be suitable for carbon steel, but it does not seem to be a good one to apply to a mixed bag containing steels varying from carbon case-hardening steel to high nickel-chromium steel, and indeed for the latter it is quite impossible to estimate the carbon content of the case accurately by this means because of the air-hardening tendencies of these high-alloy steels.

It is often difficult to assess accurately by means of the microscope the total case depth of case-

hardened steel, particularly 3% nickel steel; the personal element enters when it comes to deciding just where the low-carbon case fades into the core, but not to the extent of vitiating the results by amounts indicated in the paper.

Some experiments have been made using specimens of the same size as those used by Mr. Jenkins (10 mm. dia. × 150 mm. long), box-carburized in large industrial furnaces for periods of 10 hr. (furnace-soaked, but including heating the charge) at a temperature of 900° C. The results obtained are given below:

Steel.	Increase in Weight, ratio alloy-steel/ carbon-steel.	Total Case-Depth Measured Microscopically, ratio alloy-steel/carbon- steel.
3% Ni, En 33	0.90	0.97
Ni-Mo, En 34	0.875	1.05
Ni-Cr, En 36	1.00	1.05

In comparing alloy steels with carbon case-hardening steel En 32, total case depth has been used, for, as already pointed out, it is impossible to assess the case depth of a steel containing over 3% of nickel and 1% of chromium, by the method proposed by Mr. Jenkins. The depth at which ferrite made its appearance in the carbon steel was not very much greater than that at which it appeared in the 3% nickel steel.

The figures above convey a very different idea of the relationship between process and steel composition to that derived from Mr. Jenkins' data. The former indicate that there would usually be no serious objection to carburizing at the same time steels of the different types referred to; the latter give the distinct impression that careful segregation and batching of material according to types would be imperative when gas-carburizing, an impression which I am sure Mr. Jenkins did not intend to convey.

Recently Mr. P. F. HANCOCK and I carried out some large-scale gas-carburizing tests, and when the case depths of En 32 steel and En 36 steel were determined by chemical analysis of turnings removed from bars of 2 in. in dia., after these had been carburized and diffused together in the same charge, it was found that the carbon steel had a slightly deeper case (both total and at 0.35% of carbon) than the nickel-chromium steel (containing 3.26% of nickel, 0.81% of chromium, and 0.14% of molybdenum); but in no instance did the difference exceed 5% for the total case depth or 10% for the 0.35% carbon point.

Mr. P. F. HANCOCK (Birmingham Electric Furnaces, Ltd., Birmingham) wrote: This paper will serve a useful purpose in recording the behaviour of various gas-carburizing atmospheres. Mr. Jenkins' conclusions as to the general desirability of atmospheres free from oxidizing or

decarburizing constituents (CO_2 , H_2O , O_2) can be confirmed by this writer, who carried out a very similar series of tests some years ago, using atmospheres of butane diluted with air, partially burnt coal gas, or charcoal producer gas, and town's gas before and after purification from CO_2 , H_2O , and O_2 .

One point in this connection, however, does not seem to have been adequately emphasized by Jenkins; that is, the difference in form of any deposited carbon in the two types of atmosphere. With atmospheres free from the above impurities, the carbon is in the form of a fluffy deposit, which does not interfere noticeably with further carburization even when present in considerable quantities on the surface of the steel. With atmospheres containing appreciable amounts of CO_2 or H_2O , and particularly free O_2 , on the other hand, the deposited soot tends to be in the form of a hard, continuous shell, which may blanket the steel surface to an extent which completely prevents further carburization. The significance of this feature is fairly obvious, namely, that atmospheres of the latter type require much more stringent control in practical gas-carburizing operations, if satisfactory and uniformly carburized work is to be produced. The chemistry of carbon deposition from carburizing atmospheres would appear to be a subject on which all too little is known, and which would richly repay further study.

With regard to the relative carburizing characteristics of the three steels studied by Jenkins, there appear to be many anomalies in the recorded results; *e.g.*, Table V., line 3, where the nickel-chromium steel has a case depth of nearly twice that of the nickel steel, with the same surface carbon content, *but with only 75% of the weight*

increase. Again, the three samples shown in Fig. 12 apparently have case depths of the order of 0.020, 0.025, and 0.035 in. The case depths for these three samples given in Table V., however, are 0.036, 0.048, and 0.058 in., respectively. These discrepancies suggest considerable error, or variation, in the method of case depth measurement employed, which make conclusions difficult to draw. The general inference from Jenkins' results, however, would seem to be that there is a marked difference in the carburizing characteristics of the three steels.

This is quite at variance with results obtained by the writer, who has gas-carburized samples of plain carbon, 3% nickel, 5% nickel, and 3% nickel-chromium case-hardening steels under identical conditions for periods of 1 to 24 hr. at temperatures of 900°, 925°, 950°, 975°, and 1000° C. Case depths obtained showed that the nickel steels carburized very slightly slower, and the nickel-chromium steel faster, than the plain carbon, but the maximum variation among the four steels was in no instance greater than 5% of the total case depth, and for practical purposes the penetration rates could be assumed to be the same. These experimental results have since been confirmed by many hundreds of gas-carburizing heats under production conditions.

Recent work by Wells and Mehl, and others, on the diffusion constant of carbon in austenite, also indicates that the presence of alloying elements (at any rate in percentages up to those found in the commonly used carburizing steels) has no appreciable effect on the diffusion constant. Only slight differences in the maximum penetration rate, such as would be accounted for by varying maximum solubility of carbon, are therefore to be expected.

AUTHOR'S REPLY.

The AUTHOR replied: I would like to thank Mr. Morral for his remarks regarding American developments with liquid-carburizing baths. It would have been interesting to have had comparative data on the economic and labour aspects of the new baths with those of other carburizing processes.

The contributions of Mr. Hodgson and Mr. Hancock have very much in common, mainly in connection with the relative rates of carburization of the three steels used in the experimental work. In the first instance it seems necessary to point out that the primary object of the investigation was to study the carburizing characteristics of various

atmospheres and not the carburizing properties of different steels. Hence the carburizing temperatures used were those considered to be typical of industrial practice for the steels in question.

No particular stress was laid on the differences in carburizing rates obtained as between steels, since it was considered that such had been already well established by earlier workers and was generally recognized. It is well known, for instance, that strong carbide-forming elements tend to give an increased case depth over that of a plain carbon steel, whilst elements which do not form stable carbides have slightly the reverse effect.* The results reported in the paper confirm both this

* R. W. Schlumpf, Metals Handbook, 1939 Edition, p. 1037.

view and the following data published by American workers for steels similar to those used in the present work, carburized at 925° C. for 10 hr.*

3½% Nickel steel	0.052 in.
3% Nickel, 1% chromium steel	0.076 in.

There is scope for much more fundamental work in this connection, and the excellent research of Wells and Mehl, which incidentally does not cover the effect of chromium as suggested by Mr. Hancock, is merely the initial approach to the subject.

The "anomalies" referred to by Mr. Hodgson and Mr. Hancock would appear to be so because they do not agree with results obtained by them under entirely different conditions, on large-scale industrial plant. The fact appears to have been entirely overlooked that the present work was carried out under very precise control in the laboratory, where the duration of the carburization was confined to the actual carburizing temperatures, so that the exact carburizing time was known. On large-scale plants the period of carburization includes part of the heating and possibly the cooling cycles; the effect of this upon the ultimate case depth may vary with the type of steel and cannot be neglected, especially when the total time during the cycles, when carburizing is taking place, is an appreciable percentage of the actual time at the carburizing temperature. This is particularly so in pack-carburizing, from which certain of Mr. Hodgson's data were obtained. The comparison made, therefore, between results obtained on a practical scale and those reported in the present work are not significant in so far as the accuracy of the reported data is concerned.

It will be readily agreed that the measurement of case depth to a given carbon content by metallographic examination can give only an approximate value, especially on alloy steels. On the other hand it is noted that, in spite of his criticism of the method, Mr. Hodgson quotes results obtained by himself in this way, and presumably considers them satisfactory. The fact that he measures "total case depth" does not eliminate the difficulties inherent in the method, to which he has referred. It might be mentioned at this stage that the ratio of case depths of two different steels is not necessarily independent of the carbon concentration to which the case is measured. This will only hold if the carbon-concentration/case-depth curves in question are straight lines, with the same surface carbon content, and this of course is not so. This is a further factor which could lead to discrepancy between Mr. Hodgson's data and those reported in the paper.

In view of the foregoing it is very surprising that Mr. Hancock, referring to a supposed discrepancy between case depths given in Table V. and those shown in the corresponding photographs in Fig. 12, prefers to substitute data on the case depth of an alloy steel, carefully measured by visual examination under the microscope, by that deduced by himself from reproduced photomicrographs.

The observation made by Mr. Hancock on the differences in the nature of the soot deposited from atmospheres with and without decarburizing constituents agree with those reported in the paper. There is obviously room for much further work in this direction.

* D. K. Bullens, "Steel and Its Heat-Treatment," vol. 1, p. 257. London, 1938: John Wiley and Sons.

THE INFLUENCE OF MOVEMENT ON THE CORROSION OF METALS IN SALT SOLUTIONS AND NATURAL WATERS.*

PART I.—LOW-SPEED ROTATION OF MILD STEEL: PERIPHERAL VELOCITIES BELOW 100 FT./MIN.

By F. WORMWELL, M.Sc., Ph.D. (CHEMICAL RESEARCH LABORATORY, DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH, TEDDINGTON).

SYNOPSIS.

A rotating-specimen technique, using 1-in. dia. cylinders of mild steel at speeds up to 260 r.p.m., has been devised for investigating the influence of movement on the corrosion rates of immersed metals. Measurements of oxygen absorption, hydrogen evolution, loss of weight of metal, and depth of penetration of corrosion into the metal have been made with mild steel in 0.5N sodium chloride, "conductivity" water, a hard supply-water, and sea-water.

Evolution of hydrogen gas corresponds with a negligibly small proportion of the total corrosion of mild steel, except in sea-water, where it comprises about 5% at 43.3 r.p.m.

Corrosion-time curves for 0.5N sodium chloride are made up of linear branches, but those for conductivity water, hard supply-water, and sea-water are more complex. The maximum rate of penetration in 0.5N sodium chloride at 260 r.p.m. is about 7 mm./year.

In 0.5N sodium chloride the corrosion rate at 2 r.p.m. is three times, and that at 260 r.p.m. only twelve times, the rate in a stagnant solution. A tentative explanation is advanced.

Factors influencing the distribution of corrosion are discussed, and it is concluded that the positions of anodic and cathodic areas cannot always be located precisely. The corrosion process is, however, considered to be essentially electrochemical.

THE corrosion of iron (mild steel) and zinc in fully immersed conditions has been studied at the Chemical Research Laboratory under strictly controlled conditions, using a range of stagnant solutions and different rates of oxygen supply.¹⁻³ These rates were varied by increasing the pressure of the overlying atmosphere (oxygen or air) up to 25 atm. (oxygen) or 50 atm. (air), and by increasing the diameter of the corrosion vessels from 4.4 to 15.0 cm. It has been established that for zinc in solutions of potassium chloride or potassium sulphate of concentration greater than 0.001N, and for iron and mild steel in solutions of sodium chloride, sodium sulphate, potassium chloride, potassium sulphate, a hard public-supply water, or sea-water, the corrosion rates are determined largely by the rate of oxygen supply to the metal surface and partly by other factors, particularly the properties of the metal, solution, and corrosion products.

The series of experiments now to be described was carried out during the period 1934-40, being initiated under the direction of the late Dr. G. D. Bengough, F.R.S., and continued under Dr.

W. H. J. Vernon. A preliminary draft report was prepared by Dr. Bengough and the author in 1940, but publication (apart from several brief references^{4,5}) was deferred. The paper has been revised by the present author, who is responsible for the views and conclusions now expressed.

The investigation was designed to study the effect of the rapid supplies of oxygen made available by motion of metal and liquid. It was recognized that the problem would be complex, since motion, apart from its influence on oxygen supply, is likely to modify the effect of other factors, *e.g.*, the nature of corrosion products. Several researches on water flowing through pipes have been reported and some measurements have been conducted for limited periods with rotating specimens,⁶⁻¹¹ but no systematic study on the lines to be described has been found in the literature.

EXPERIMENTAL.

Specimens.

The metal used was normalized mild steel,[†] similar to that employed in earlier work.¹² The

* Received March 27, 1946.

† The analysis of the steel was as follows: 0.14%C, 0.13%Si, 0.39%Mn, 0.022%S, 0.034%P, 0.24%Ni, trace Cr, 0.07%Cu.

form of specimen adopted was a cylinder, 2.5 cm. in dia. and 1.9 cm. long, turned to size with a fine cut on a precision lathe; the exposed area (15 sq. cm.) consisted of the curved surface only. The weight and diameter of each specimen were measured initially. At the end of an experiment the corrosion products were usually removed by brushing with a stiff bristle brush, and were collected for estimation of ferrous and ferric iron. With specimens corroded in hard supply-water or sea-water, however, it was necessary to remove deposits of carbonate by a short immersion in acid or by cathodic treatment in sodium cyanide solution. Specimens were then reweighed after

	Ca.	Mg.	CO ₂ .	SO ₄ .	Cl.	SiO ₂ .
Parts/100,000	11.8	2.0	18.7	3.2	5.1	2.5
pH	.	.	.	7.5-8.0		
Total solids	.	.	.	36		
Free CO ₂	.	.	.	0.5		
Total hardness	.	.	.	32		
Temporary hardness	.	.	.	24		

Rotating-Specimen Assembly.

The procedure adopted was to spin a cylindrical specimen in the corroding liquid contained in a closed vessel and to measure the progress of corrosion by daily determination of oxygen absorbed and hydrogen evolved. This method—an adaptation of that previously used for experi-

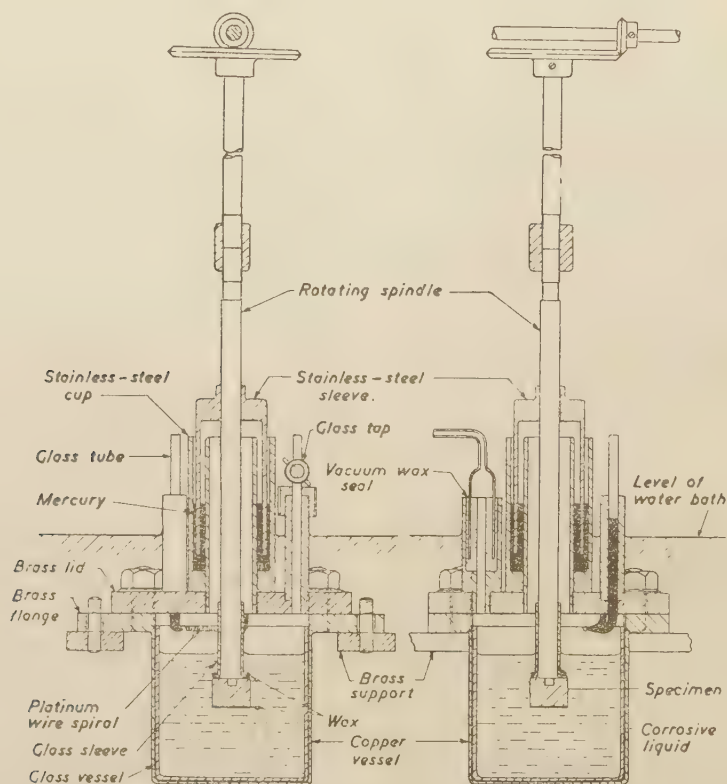


FIG. 1.—Rotating-Specimen Assembly in Sealed Vessel. Gas-absorption method.

drying with filter paper, followed by storage for 24 hr. in a desiccator. The depth of penetration of corrosion was finally measured as described later in the paper.

Solutions.

All solutions were prepared from Analar-grade chemicals in high-quality "conductivity" water (electrical conductivity less than 0.1×10^{-6} mho when in contact with purified air). Filtered sea-water was supplied by the Marine Biological Laboratory, Plymouth. A hard public-supply water was used in some experiments. A typical analysis of the water was as follows:

ments in stagnant solutions¹—was chosen because it provides information on the relative importance of hydrogen-gas evolution in relation to the influence of motion, a point that does not appear to have received attention in the literature.

Fig. 1 is a scale drawing of the apparatus. Six units were constructed, each with a vertical spindle of stainless steel, held in two plain bearings (not shown in the figure) and connected by suitable gears to an overhead horizontal shaft driven through a reduction gear by an electric motor. The specimen, with a screw-tapped hole in the top, was fixed to the bottom of the vertical spindle, the lower part of which was shielded by a glass sleeve sealed to the specimen with gutta-

percha/paraffin-wax mixture. The bottom surface of the specimen was also covered with wax, so that corrosion was confined to the vertical cylindrical surface of the specimen that was moved through the liquid at a known speed.

The specimen was immersed with its upper edge 1.5 cm. below the surface of the corroding liquid (500 ml.); this liquid was contained in a resistance-glass vessel, 9.4 cm. in internal dia. and 10.0 cm. deep, as used in earlier work. Hydrogen gas was estimated by passing an electrical current through the platinum-wire spiral shown in Fig. 1. The corrosion vessel was made gas-tight by a lead washer which bedded into a groove cut in the flange of the copper pot when the six hexagonal nuts were tightened on the studs fixed to the pot.

TABLE I.—*Calculated and Observed Losses of Weight.*

Experiment No.	Speed, r.p.m.	Time, days.	Solution.	Oxygen Absorbed, ml.	Hydrogen Evolved, ml.	Amount of Ferrous Iron in Product, %.	Loss of Weight, g.	
							Observed.	Calculated.
106	2	289	0.5N NaCl	569.5	24.6	9.95	1.204	1.604
97	7	132	"	327.9	3.9	11.6	0.850	0.940
105	11	295	"	844.2	14.6	4.7	2.139	2.395
18	13	159	"	449.1	3.6	5.9	1.353	1.280
11	65	126	"	532.8	11.3	15.5	1.639	1.633
22	86.7	111	"	481.9	12.8	16.0	1.427	1.482
7	130	133	"	753.7	20.7	19.3	2.347	2.354
31	260	112	"	1581	10.6	9.6	4.818	4.980
27	65	175	Conductivity water	218.6	6.1	26.4	0.599	0.729
25	130	161	" "	181.0	4.7	24.4	0.557	0.607
117	7	218	Hard supply-water	418.2	0.65	26.9	1.338	1.320
29	43.3	167	" "	378.1	2.0	26.8	1.098	1.268
30	86.7	162	" "	369.6	3.6	34.6	1.248	1.279
111	130	140	" "	227.9	3.9	14.0	0.686	0.649
108	260	230	" "	398.6	7.7	41.0	1.060	1.190
19	43.3	150	Sea-water	300.4	22.2	21.1	0.863	0.901

Each corrosion vessel was supported on horizontal brass strips in a water thermostat at $25^{\circ} \pm 0.05^{\circ} \text{C}$.

Method of Measuring Corrosion.

Readings of oxygen absorption* were taken daily and of hydrogen evolution every two or three days, after which the air in the apparatus was swept out for 15 min. by drawing air saturated with water vapour through the glass taps in the lid of the corrosion vessel. The gas readings were corrected for changes of barometric pressure, as these affected the pressure in the vessel owing to movement of the mercury seal. A further correction to oxygen-absorption values was necessitated by a "blank" absorption of oxygen (in the absence of a corroding specimen) probably due to oxidation of the mercury in the seals. Although the mercury was covered with a layer of liquid paraffin, a steady absorption of 0.25 ml./day was measured.

* Since the volume of air space above the liquid was 400 ml., the decrease in partial pressure between gas readings was usually in the range of 0.3–2.0%, thus involving very small corrections.

† Results of extended tests will be reported later.

At the end of each experiment the loss of weight of metal was calculated from the corrected volumetric readings and a knowledge of the percentage of ferrous iron in the corrosion products. Comparisons with observed losses of weight are given in Table I., from which it is seen that agreement is reasonably good. Any experiments showing lack of agreement were rejected as untrustworthy.

Simplified Technique for Loss-of-Weight Tests.

In later work, experiments have been conducted in a vessel (Fig. 2) provided with a lid carrying tubes open to the air, but avoiding exposure of the solution to currents of air at a lower temperature. This will be referred to later as the "covered" as distinct from the "sealed"

vessel of Fig. 1. Replacement of solution can be made by withdrawal through glass tubes sliding inside the brass tubes in the lid. Evaporation occurs to a limited extent, but can be closely estimated and made good from time to time by additions of distilled water (previously brought to thermostat temperature). Experimental results (discussed later) compare favourably with those obtained by the more elaborate technique.

Testing of Sheet Specimens.

A disadvantage of the two techniques already described is that one spindle carries only one specimen, which must be turned to cylindrical form. This is convenient if metal is available as round bar, but tests are often required on material in sheet form. Preliminary experiments† have been carried out with a simple ebonite holder. Six specimens, $3.0 \times 1.5 \times 0.3 \text{ cm.}$, fit tightly

into slots in the periphery of the holder, which is 2 in. in dia.; a coating of chlorinated rubber on the

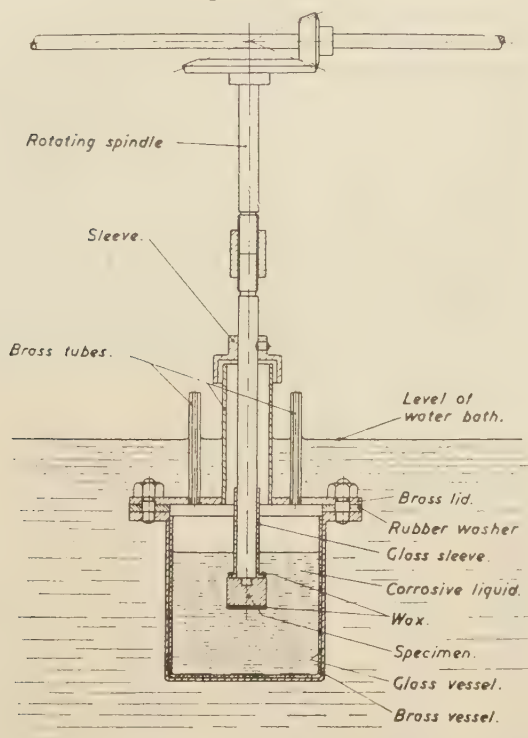


FIG. 2.—Simplified Rotor Assembly in Covered Vessel. Loss-of-weight method.

back and edges of the specimens is sufficient to hold them in position. The holder screws on the lower end of a vertical ebonite spindle.

EXPERIMENTAL RESULTS.

Form of Corrosion-Time Curves in 0.5N Sodium Chloride.

The corroding liquid chosen for the main series of experiments was 0.5N sodium chloride; this

was on account of the considerable amount of corrosion data already accumulated for this solution, which corresponds roughly in salt concentration to that of sea-water.

Corrosion-time curves (calculated from gas readings) showing reproducibility of results are given in Fig. 3. Corrosion rates are variable in the early stages of duplicate experiments, *e.g.*, R9 and R18, but the general form of the curves is similar to that obtained in stagnant conditions. Initial corrosion rates corresponding to the initial "a" branches of the curve¹³ are maintained for only 5–10 days, after which slightly lower (but well-maintained) rates are observed, corresponding to the second, and more characteristic, "b" branch in stagnant solutions. The rates are always greater in moving than in stagnant salt solutions.

Fig. 4 includes comparative curves obtained at 130 r.p.m. in sealed (Fig. 1) and covered (Fig. 2) vessels, respectively. There is good agreement in 100-day tests, especially considering that with the sealed-vessel technique the curve represents successive readings on a single specimen, whereas with the simpler apparatus the curve is built up from loss-of-weight figures for separate specimens. This gives confidence in the simplified technique.

The curves in Fig. 5 show, at the higher speeds, steeper branches in the later stages, indicating considerable increases in corrosion rates. The increase occurs after a shorter period the higher the speed of rotation, *e.g.*, after about 50 days or less at 260 r.p.m. and after about 100 days at 130 r.p.m.; this is probably due to the effect of rust nodules in increasing the turbulence in the solution.

Comparative results from the gas-absorption (sealed vessel) * and loss-of-weight (covered vessel) methods are given in Fig. 6 for a speed of 260 r.p.m. Good agreement is obtained during the first 30 days, but variable results are characteristic of the later stages whichever method is used, because on different specimens the increase in

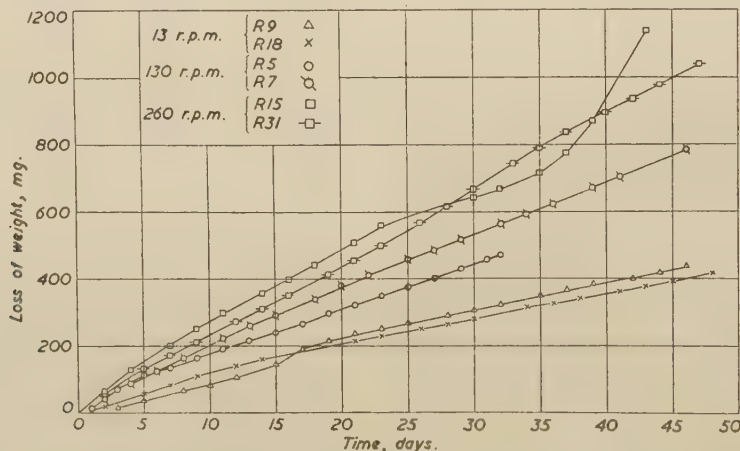


FIG. 3.—Corrosion-Time Curves Showing Reproducibility of Results: Mild steel in 0.5N sodium chloride.

* See curves for specimens R15 (Fig. 3) and R31 (Figs. 3 and 5).

turbulence (due to nodule formation) occurs at different corrosion periods.

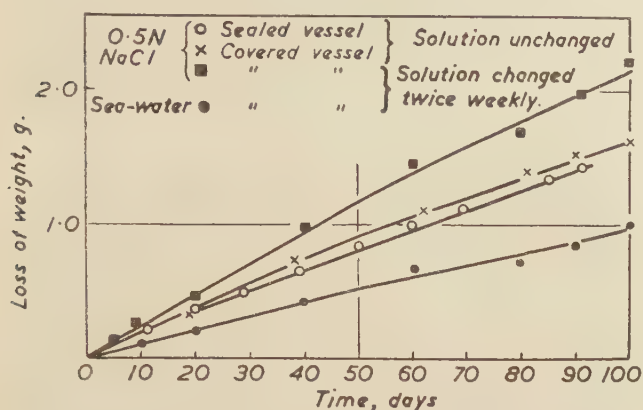


FIG. 4.—Corrosion-Time Curves at 130 r.p.m. for 0.5N Sodium Chloride and Sea-Water in Sealed and in Covered Vessels. Effect of renewal of solution.

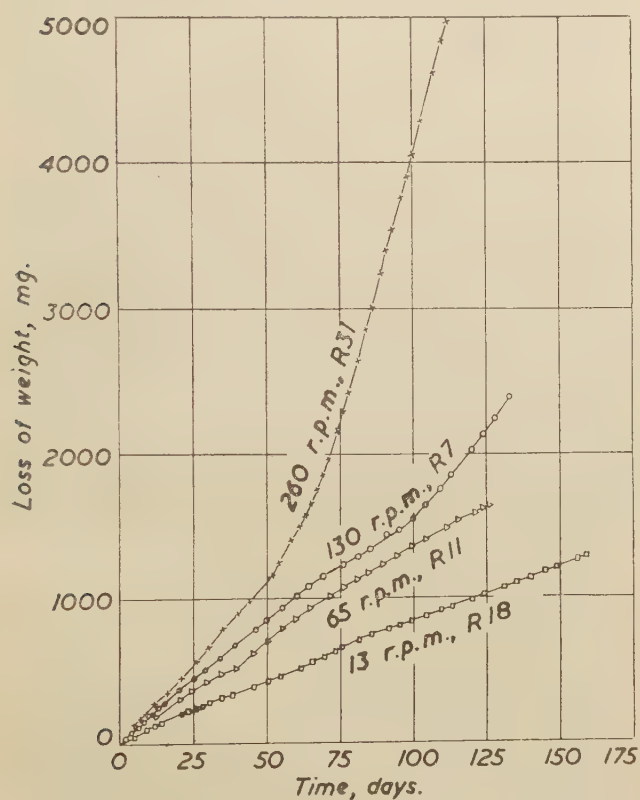


FIG. 5.—Corrosion-Time Curves for Mild Steel in 0.5N Sodium Chloride, showing increased corrosion rates in later stages at higher speeds.

Influence of Speed of Movement in 0.5N Sodium Chloride.

Corrosion rates corresponding to the "b" branches of the corrosion-time curves appear to be most characteristic of the experimental conditions. These rates are plotted against speed of rotation in Fig. 7, each point representing the average of

duplicate or triplicate experiments. The rate for zero movement is taken from earlier measurements on discs of the same surface area (15 sq. cm.) but exposed in stagnant solution. It is clear

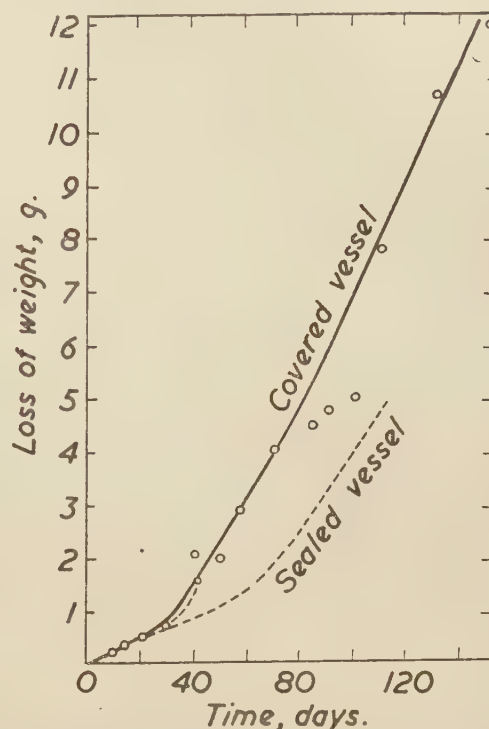


FIG. 6.—Corrosion-Time Curves; 0.5N sodium chloride in sealed and in covered vessels. At 260 r.p.m.

that low speeds of rotation are proportionately more effective than higher speeds, *e.g.*, the rate is approximately trebled at 2 r.p.m. but is increased only 12-fold at 260 r.p.m. (68 ft./min.). An

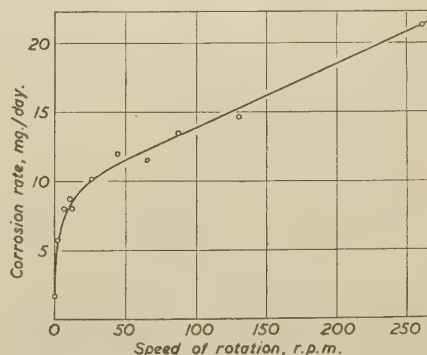


FIG. 7.—Increase in Corrosion Rate with Speed of Rotation; 0.5N sodium chloride.

interpretation of these results will be discussed later.

Corrosion Distribution in 0.5N Sodium Chloride.

Examination of a large number of specimens after corrosion tests of different durations and at various speeds showed the following sequence of

events: First, a differentiation of the metal surface into well-marked, attacked (presumably anodic) areas, and unattacked (presumably cathodic) areas; the latter gradually became tarnished (brown, later turning black) and steadily diminished in size, owing to encroachment from the boundaries. Corrosion also started at numerous points within these (originally protected) areas, and gradually spread until no unattacked surface remained. These events took place more rapidly at higher speeds of rotation.

The gradual changes in corrosion distribution could not be correlated with observable changes in corrosion rates; these remained constant over periods of 40 days or more (Figs. 3 and 5) during which time considerable alterations of anode-cathode distribution must have occurred.

The high corrosion rates in later stages persisted after the complete disappearance of the original surface and, therefore, of identifiable cathodes, and, furthermore, in spite of the accumulation of masses of corrosion products over the whole surface of the metal. These products consisted mainly of a layer of ferroso-ferric oxide next to the corroded metal, with soft and powdery ferric oxides overlying the primary layer. The rust closely resembled that observed in stagnant solutions.

Corrosion in "Conductivity" Water.

Corrosion rates of mild steel in conductivity water were variable and, at times, high (Fig. 8).

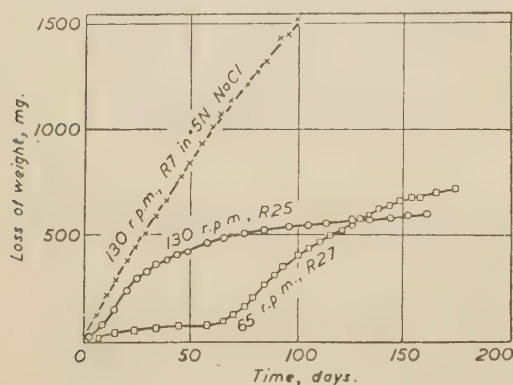


FIG. 8.—Corrosion-Time Curves; conductivity water.

After a period of about 150 days, the rates at 65 and 130 r.p.m. were similar, suggesting that they were largely independent of the rate of oxygen supply. In both experiments corrosion spread over a large proportion of the metal surface, and at the higher speed the protected areas were reduced to a large number of small islands.

Corrosion in a Hard Public-Supply Water and Sea-Water.

At a speed of 43.3 r.p.m. corrosion rates* were

* Based on loss-of-weight/time curves (not reproduced here).

very similar in the hard supply-water and natural sea-water for the duration of the tests (100 days). In the supply-water at other speeds between 7 and 260 r.p.m. corrosion-time curves showed increased rates after about 50 days, followed by pronounced decreases, which were more rapid at higher speeds.

Effect of Renewal of Solutions.

A factor that becomes important in long-continued experiments with such natural waters is the effect of changes in composition of the solution. This does not arise with iron or steel corroding in salt solutions, such as 0.5N sodium chloride, since the chloride is not used up in the corrosion process. In the hard supply-water and in sea-water, on the other hand, it is known that calcium and magnesium compounds are deposited on the cathodic areas owing to the local increase of alkalinity. The influence of these deposits is likely to be more marked if the concentration of calcium and magnesium salts is maintained by renewal of the water.

It was found possible, using the sealed-vessel technique, to change the water at weekly intervals simultaneously with renewal of air inside the corrosion vessel, by withdrawing the water through one of the glass tubes inserted in the lid of the apparatus (Fig. 1). The procedure was, however, difficult and caused disturbance of the gas pressure during the following 24 hr., presumably because the water was not in true equilibrium with the atmosphere. Corrosion-time curves constructed from the oxygen-absorption and hydrogen-evolution readings were found to be appreciably in error, the calculated loss of weight being much higher than the loss measured directly. The actual losses are compared with those obtained in earlier tests (water not renewed) in Table II.; this comparison shows

TABLE II.—Effect of Renewal of Hard Supply-Water.

Speed, r.p.m.	Loss of Weight, g.			
	Water Not Renewed.		Water Renewed.	
	130 days.	175 days.	130 days.	175 days.
86.7	1.16	1.30	0.35	0.37
260	1.01	1.12	0.35	0.45

that renewal of water has reduced corrosion to about one-third. This result is undoubtedly due to the restraining effect on the cathodic (and possibly also on the anodic) reaction of increased deposits of calcium carbonate.

The influence of renewal of liquid is shown in Fig. 4 for 0.5N sodium chloride. The increased

corrosion rate may here be due to the disturbance of experimental conditions, leading to increased supply of oxygen, or to the removal of accumulations of corrosion products. It has been verified by analysis that chloride concentration is unchanged after corrosion periods of at least 50 days.

Fig. 4 also gives a comparative curve for natural sea-water, the solution being renewed twice weekly as for sodium chloride. The results confirm the higher corrosion rate in 0.5*N* sodium chloride that has been observed in other work.

Evolution of Hydrogen Gas.

In all the experiments described in this paper, except those in sea-water, the amounts of corrosion corresponding to hydrogen evolution were of the same order as those in stagnant solutions and represented negligibly small proportions of the corrosion due to oxygen absorption. In sea-water, the rate of hydrogen evolution was actually less than that in stagnant conditions but nevertheless accounted for an appreciable proportion (about 5% at 43.3 r.p.m.) of the total corrosion.

Depth of Penetration of Corrosion.

Under many industrial conditions the loss of weight of metal per unit area is of less importance than the depth of penetration of corrosion. Measurements of this depth have therefore been made on selected specimens by carefully turning down the surface (*a*) until the metal standing in relief at protected areas is removed down to the level of the high spots on the corroded areas, and (*b*) until the entire corroded areas have just disappeared. The mean of the depths (*a*) and (*b*) is taken as the average depth of penetration, and the depth of (*b*) gives the deepest penetration.¹⁴ Results for typical specimens used in the gas-absorption series of tests are given in Table III.

TABLE III.—Depth of Penetration of Corrosion

Experiment No.	Speed, r.p.m.	Time, days.	Solution.	Depth of Penetration, mm.	
				Average.	Deepest.
106	2	289	0.5 <i>N</i> NaCl	0.13	0.42
97	7	132	"	0.09	0.14
28	260	42	"	0.26	0.66
27	65	175	Conductivity water.	0.05	0.16
29	43.3	167	Hard supply-water.	0.095	0.225
19	43.3	150	Sea-water	0.15	0.28

The deepest penetration is appreciable even in conductivity water, and that in the hard supply-water is not greatly below the figure for sea-water

at 43.3 r.p.m. In 0.5*N* sodium chloride the figure of 0.42 mm. at 2 r.p.m. and 289 days is exceeded by that of 0.66 mm. at 260 r.p.m. and 42 days.

Penetration-time curves obtained by the sim-

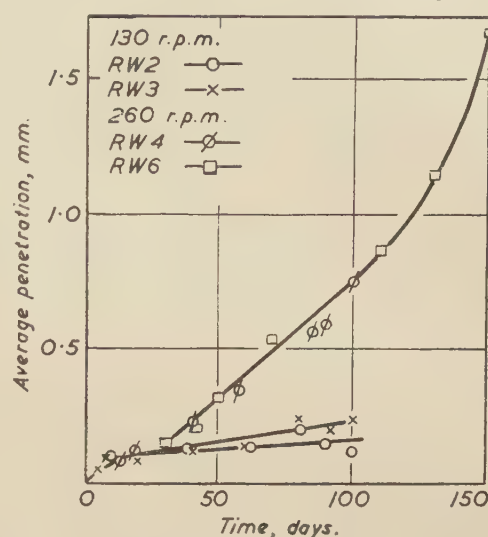


FIG. 9.—Average-Penetration/Time Curves: 0.5*N* sodium chloride at 130 and 260 r.p.m.

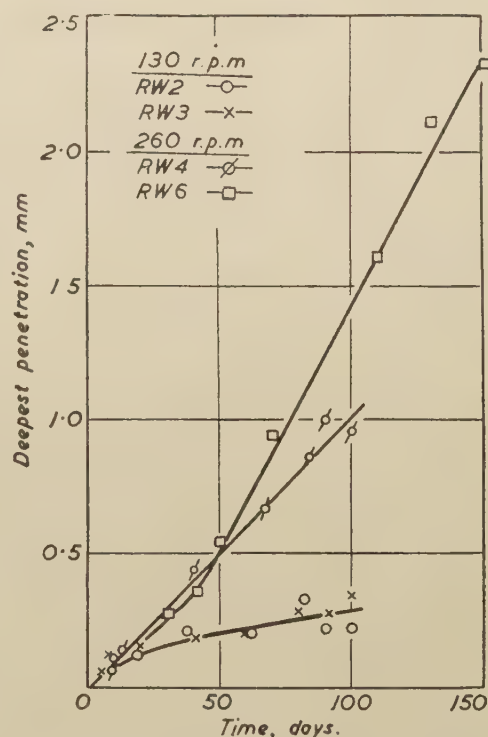


FIG. 10.—Deepest-Penetration/Time Curves: 0.5*N* sodium chloride at 130 and 260 r.p.m.

plified technique in 0.5*N* sodium chloride at 130 and 260 r.p.m. are given in Figs. 9 and 10. As might be expected, the individual results often show appreciable scatter, but there is no doubt as to the general trend of the curves. The

increase in corrosion rate at 260 r.p.m. is again reflected in the curves, but at different times according to whether the average or the deepest penetration is measured. Since the corroded area is increasing with time, it is not surprising that the increase in loss-of-weight rate after about 50 days at 260 r.p.m. is not reflected in the curve for average penetration. The increase in slope of this curve is delayed until about 110 days, when all the surface area of the specimen is usually corroded.

The rates of penetration at 260 r.p.m. are very high and from present evidence show no sign of decreasing with time. The values for the earlier and later stages, calculated from the slopes of curves in Fig. 10, are 3.4 and 6.9 mm./year, respectively. Corresponding rates of corrosion in sea-water are not available but from other unpublished work it is known, both for lower and higher rates of movement, that corrosion in sea-water is much less than in 0.5*N* sodium chloride. Evidence indicates that the lower rate in sea-water is due to the deposition of magnesium and calcium compounds from the sea-water owing to a rise of pH at cathodic areas.

DISCUSSION OF CORROSION MECHANISM.

Corrosion Rate.

The observed increase in corrosion rate in 0.5*N* sodium chloride, as the speed of rotation is increased, is no doubt due largely to the increased rate at which oxygen is brought to the metal by liquid movement. The form of the corrosion-rate/speed-of-rotation curve in Fig. 7 may be compared with curves obtained by Abramson and King¹⁵ for the rate of dissolution of iron in acids, where the diffusion rate of acid was a controlling factor. It is evident that, with higher speeds of rotation, a given increment of speed is less effective in increasing diffusion rates. In the present work, corrosion rapidly produces roughening of the metal surface and it is probable that, even at the lowest speeds, turbulent motion of the liquid occurs. This would account for the marked increase in corrosion rate at 2 r.p.m. as compared with stagnant conditions. Further increments of speed introduce a gradually increasing degree of turbulence, leading to increased corrosion rates as represented by the later part of the curve in Fig. 7. Another factor that increases the rate of transport of oxygen from the air-liquid interface is the general stirring of the liquid. The relative contributions of the different factors can be estimated only by further work, using modifications such as the introduction of baffles to prevent the general movement of the liquid. From Fig. 7 the following relation can be deduced for speeds above 50 r.p.m.:

$$\text{Corrosion rate (mg./day)} = 9.2 + 0.046 S$$

where S = speed in r.p.m. From this equation, the calculated corrosion rate at 1500 r.p.m. for a mild-steel surface of area 1 sq. in. at the periphery of a 5-in. dia. rotor (assuming corrosion rate is a function of peripheral speed) is 152 mg./day. The rate observed in (unpublished) work at the Chemical Research Laboratory is of the order of 100 mg./day for the first 15 days. It appears, therefore, that the linear branch of Fig. 7 is not maintained at very high speeds of movement.

If the logarithm of corrosion rate is plotted against the logarithm of speed, the points lie on or close to a straight line up to a speed of 130 r.p.m. The corrosion rate at 260 r.p.m. is, however, much higher than that given by the relation covering the range of speed below 130 r.p.m., *viz.*:

$$\log_{10} V = 0.70 + 0.225 \log_{10} S$$

where V = corrosion rate in mg./day and S = speed of rotation in r.p.m. It would appear that for speeds from 2 to 130 r.p.m., $V = KS^n$, where $K = 5.0$ and $n = 0.225$. The form of this equation is similar to that obtained by Nernst and many subsequent workers on solution rates, and is ascribed to the reduction in thickness of the diffusion layer caused by increased liquid movement. The value of n was given as two-thirds by Nernst and Merriam¹⁶ and also by Brunner.¹⁷ Eucken¹⁸ deduced by hydrodynamic arguments a figure of one-third, whilst Coates¹⁹ has obtained a value of 0.3. On the other hand, Kimball²⁰ prefers a different relationship based on the assumption that the thickness of the diffusion layer is inversely proportional to the stirring rate. It seems clear that the precise form of the solution-rate/speed relation varies with the nature of the solid and liquid components being studied. Considering the conditions of the present investigation, *viz.*, the corrosion of steel in neutral salt solutions, the influence of movement cannot be accounted for solely on the diffusion-layer mechanism as applied to the transport of oxygen through the solution to the metal surface.

Apart from the rate of oxygen supply, which has been studied especially in this research, the other principal factors affecting corrosion rates of mild steel in neutral salt solutions are:

- (1) Electrochemical properties of the metal,
- (2) Nature of ions in solution,
- (3) Nature of corrosion products, and
- (4) Rate of movement of the liquid.

Some of these factors are interdependent; for example, (3) is a function of (1), (2), and (4).

The influence of the electrochemical properties of the metal has not been studied in the present investigation, although evidence has been obtained that the corrosion rate of electrolytic zinc in 0.5*N* sodium chloride at 11 r.p.m. is less than that

of mild steel. This suggests that the corrosion products on zinc exert a restricting effect which masks the electronegative properties of the metal. Considering the influence of the nature of the ions, the differences in corrosion rates are too large to be accounted for by differences in solubility of oxygen in the solutions, and are therefore to be ascribed to factor (3). Experimental evidence indicates that the nature of the obstructive films or masses of corrosion products differs, for a given metal, according to the constituents of the solution and the speed of movement.

The electrolytic conductivity of the solution appears to have a negligibly small direct effect on corrosion rates. Thus, specimens rotated in conductivity water corroded for several days at a rate not far below that in 0.5*N* sodium chloride (Fig. 8), although the respective specific conductivities are about 1.0×10^{-6} mho (water in equilibrium with room atmosphere) and 4.7×10^{-2} mho, respectively. Possibly, a close spacing of electrodes occurs in solutions of low conductivity, depolarization taking place mainly near the anodes. For example, the maximum observed rate of about 15 mg./day in conductivity water corresponds to a working e.m.f. of 1 V. with electrodes of 7.5 sq. cm. in area and 2×10^{-2} cm. apart. Alternatively, the rate may be controlled²¹ by the oxidation of a ferrous hydroxide film formed by discharge of OH⁻ ions at the anode. The oxidation rate will then be determined by the rate of arrival of oxygen.

Corrosion Distribution.

The gradual (but finally complete) disappearance of all unattacked areas requires explanation. Evans and Hoar²² have shown that in 0.5*N* sodium chloride the initial corrosion rate of partly immersed mild steel corresponds closely to the current passing between well-defined, attacked (anodic) and unattacked (cathodic) areas. It is known that alkali is produced and tends to repress attack at cathodes, while soluble ferrous chloride is formed at anodes and so tends to assist continued corrosion there by neutralizing alkali diffusing from cathodic areas. This occurs early in the corrosion process and it might be expected that corrosion would always continue at the well-established anodes, forming pits or basins surrounded by comparatively unattacked metal. Actually, the clear-cut distinction between anodic and cathodic areas occurs only during the initial stages of corrosion of mild steel in the conditions now under discussion. Later, the original cathodic areas become attacked to such an extent that corrosion tends to overtake that at the original anodes. This would imply that at some stage there is a reversal in the direction of current. The phenomena are similar in both stagnant and

moving solutions but the sequence of changes is much more rapid in the latter case.

All corroded areas, finally comprising the whole specimen area, become covered with stable, black, magnetic oxide which is gradually built up into a coherent layer that is sometimes removable intact from the metal. Although the layer is apparently continuous and may reach a thickness of 0.5 mm. or more in a year, it must be porous, for both black and brown oxides are deposited on the outside of it. Possibly oxygen can proceed inwards and ions outwards through microscopic channels, though depolarization may occur on the outside of this layer, which will then function as a "metallic" conductor.²³ On this view, the magnetite-covered metal will present a "compromise potential" owing to local action through the layer, the metal at the bottom of a pore in the oxide acting as anode and the exterior of the layer as cathode. This hypothesis avoids the difficulty of postulating a rapid movement of oxygen through the layer to explain the linear form of the corrosion-time curves. Owing to the breakdown (already described) of the tarnish film on the original cathodes, the metal thus exposed is electronegative to the neighbouring tarnish film and also to the thick magnetite layer, and therefore can corrode sufficiently fast to compensate for any reduction in rate at the original anodes. This would account for the striking observation that the corrosion rate of the specimen as a whole is not lowered by the presence of a thick, apparently compact, layer of magnetic oxide. No doubt, also, the positions of the pores in the layer will change with time, owing to reinforcement from below and consequent disturbance of the structure. This is consistent with the relatively even corrosion of the surface after long periods in sodium chloride solutions. The metal is finely reticulated as if attacked by dilute acid.

From the preceding discussion, and in conformity with earlier results²⁴ in stagnant conditions, it appears that the distribution of anodes and cathodes on metal completely immersed for long periods in salt solutions is by no means clear-cut, nor is it constant with time. When the surface of mild steel shows the usual distribution of well-marked attacked and protected areas characteristic of the early stages of corrosion, it is commonly assumed that all cathodic oxygen consumption occurs at the electropositive (unattacked) areas. The fact that these gradually decrease in size and ultimately disappear without any accompanying decrease of corrosion rate (and sometimes with an increase) proves that cathodic depolarization must occur, at least in the later stages, over corroded areas. The "oxygen-catchment" area must be at least maintained and, possibly, increased. It is not known whether metal dissolution and cathodic depolarization respectively can occur at

contiguous (or not far distant) atoms, but it is probable that anodic and cathodic areas are constantly changing and are so closely intermingled in the later stages of corrosion as to be indistinguishable by visual (and possibly also by electrochemical) observations.

SUMMARY AND CONCLUSIONS.

Corrosion-time curves obtained from tests in 0.5*N* sodium chloride comprise linear branches, generally showing a downward inflection after 5–10 days (depending on the speed). They show a pronounced upward inflection after 50 days or less at 260 r.p.m., and after about 100 days at 130 r.p.m. This increase in corrosion rate is considered to be due to increased supplies of oxygen caused by increased turbulence of the liquid; this arises from the development of large rust nodules on the specimen. In conductivity water, hard supply-water, and sea-water, the shapes of the curves are more complex, and further work is required to establish the typical behaviour in these solutions. A twice-weekly renewal of hard supply-water reduces the corrosion to about one-third of that observed in unchanged water. This conforms with existing knowledge of the inhibiting effect of calcium carbonate (deposited cathodically) on corrosion of steel in natural waters.

Evolution of hydrogen gas accounts for a negligibly small proportion of the total corrosion of mild steel, except in sea-water, where it comprises about 5% at 43.3 r.p.m.

The maximum rate of penetration of corrosion in 0.5*N* sodium chloride at 260 r.p.m. is about 7 mm./year; it is 3.4 mm./year in the early stages.

In 0.5*N* sodium chloride a given increase in speed is much more effective at lower speeds; e.g., at 2 r.p.m. the corrosion rate is three times, and at 260 r.p.m. it is twelve times, that observed in a stagnant solution. An interpretation of this relationship is tentatively advanced.

Factors influencing the distribution of corrosion are discussed, and it is concluded that the positions of anodic and cathodic areas cannot always be precisely located, especially at an advanced stage in the corrosion process when the whole area of a specimen has become corroded. There is little doubt, however, that the corrosion process is essentially electrochemical (except, possibly, in conductivity water). The compact layer of magnetite formed in later stages may act as a cathode.

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THE PROTECTION OF IRON AND STEEL BY METALLIC COATINGS.*

RESULTS OF FIVE YEARS' EXPOSURE TESTS.

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Sub-Committee).*

(Figs. 1 to 19 = Plates XXXV. to XL.)

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SYNOPSIS.

An account is given of the observations made to date on the behaviour of a wide range of protective coatings applied to mild steel exposed to field corrosion tests as part of the investigations of the Protective Coatings Sub-Committee. These results cover periods of up to 5 years in the case of atmospheric exposure and of 2 years in that of immersion in sea-water. The coatings under investigation are aluminium, cadmium, lead, tin, and zinc, together with 82/18 cadmium-zinc alloy and 88/12 lead-tin alloy ("terne"). These were applied in one or more of three standard thicknesses, nominally 1, 3, and 5 mils, by a wide variety of processes, including cementation, electrodeposition, hot-dipping, and spraying. In the last case, specimens were prepared by three types of metal-spraying process, namely, the molten-metal pistol, the powder pistol, and the wire pistol.

A summary of the results will be found in the text.

1.—INTRODUCTION.

ALTHOUGH painting is at present and in all probability will remain the most common of the protective measures for preventing the corrosion of iron and steel, within the last decade or so there has been a considerable expansion in the use of other methods of protection, notably by metallic coatings of less corrodible non-ferrous metals. In addition to the older well-established methods, such as hot-galvanizing or tinning, the field of usefulness of metallic coatings as applied to iron and steel has been materially widened both by the development of new and the improvement of older methods of application, such as metal spraying in the first case, or electrodeposition in the second; moreover, some new metals or alloys have become available for protective coatings, of which aluminium is the outstanding example. Consequently, in 1938 the Protective Coatings (Corrosion) Sub-Committee* decided that it would serve a useful purpose if it were to undertake a series of systematic exposure tests on as wide a range as possible of metallic protective coatings for iron and steel.† This step was felt to be the more desirable because, largely owing to the rapidity with which advances were being made in this field, but partly because the interest of individual investigators had been necessarily confined to a limited section of it, no such systematic comparison had hitherto been attempted either in this country or elsewhere.‡

The experimental scheme drawn up by the Protective Coatings (Corrosion) Sub-Committee was duly executed. The necessary steel was made in October, 1938, most of the coatings were applied in the period May–December, 1939, and specimens for atmospheric-exposure tests were exposed at three stations in this country during July and August of 1940.

Atmospheric-corrosion tests on other sets of

specimens exposed overseas were begun during 1941 and 1942. In addition, two additional sets were immersed in sea-water in 1941.

This report is therefore concerned with the results to date of atmospheric-exposure and sea-water immersion tests conducted on a range of protective metallic coatings applied to mild steel. These results cover a period of approximately five years' exposure in the case of atmospheric-corrosion tests in this country and of correspondingly shorter periods for the specimens exposed overseas. The main set of sea-water immersion specimens has been examined after two years; some of the specimens have been re-immersed for a further period. Other results of the sea-water immersion tests have already been given in the First Report of the Marine Corrosion Sub-Committee.¹

2.—ACKNOWLEDGMENTS.

The Protective Coatings Sub-Committee decided at the initiation of this work that it was most desirable that, wherever possible, the test-coatings should be applied under industrial conditions at works where the different processes were in use. This decision has been implemented as a result of the willing and enthusiastic collaboration received from a number of firms and research institutions connected with protective coatings and processes. All of these, when approached, expressed their readiness to assist in the provision of the coatings or protective schemes required and have provided facilities for the investigators to visit their works or laboratories to record on the spot the necessary experimental observations. Consequently, before proceeding to discuss the experiments and the results obtained it is fitting to record acknowledgments to all those who have assisted the Sub-Committee in this and in other ways. In addition to specific acknow-

* The Protective Coatings (Corrosion) Sub-Committee is a Sub-Committee of the Corrosion Committee. The latter in turn is a joint research Committee of The Iron and Steel Institute and the British Iron and Steel Research Association.

† Tests on a number of non-metallic coatings other than paint were undertaken at the same time, but these will be described in a separate paper.

‡ The nearest approach to this are the investigations of Committee A5 (Sub-Committee VIII.) of the American Society for Testing Materials, which are concerned with exposure tests of various grades of hardware protected by different metallic coatings as applied commercially.

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3.—EXPERIMENTAL DETAILS.

List of Symbols.

The symbols used throughout the paper have been collected together for convenience and are presented below :

<i>W</i>	Weight of coating, g./specimen.
<i>w</i>	Weight of coating, oz./sq. ft. of surface.
<i>x</i>	Grade "excellent," <i>i.e.</i> , no sign of breakdown of coating.
<i>f</i>	Grade "fair," <i>i.e.</i> , coating showing signs of breakdown.
<i>o</i>	Grade "failed," <i>i.e.</i> , 5% or more of the steel rusted.
<i>T_m</i>	Coating thickness, mils. Average value obtained by electromagnetic meter (<i>see</i> Appendix B).
<i>L_f</i>	Life of coating to grade "fair," years. Mean value for the front and back surfaces.
<i>L_o</i>	Life of coating to grade "failed," years. Mean value for the front and back surfaces.

(a) *The Experimental Programme.*

A list of the metallic coatings and the methods of application which constitutes the general scheme of the investigations undertaken by the Protective Coatings Sub-Committee is presented below ; particulars of the preparation of the various specimens will be found in Appendix A :

Reference No.	Coating Metal or Alloy.
(0)	No coating.
(1)	Aluminium.
(2)	Cadmium.

Reference No.	Coating Metal or Alloy.
(3)	Cadmium-zinc (82/18).
(4)	Zinc.
(5)	Lead.
(6)	Lead-tin (88/12).
(7)	Tin.
Method of Application.	
(0.0)	Cemented.
(0.1)	Electrodeposited.
(0.2)	Electrodeposited (cyanide bath).
(0.3)	Electrodeposited (cyanide bath with chromate rinse).
(0.4)	Hot-dipped (firm A).
(0.5)	Hot-dipped (firm B).
(0.6)	Hot-dipped with heat-treatment.
(0.7)	Sprayed with molten-metal pistol.
(0.8)	Sprayed with powder pistol.
(0.9)	Sprayed with wire pistol.
Nominal Thickness of Coating.*	
(0.01)	1 mil.†
(0.02)	3 mils.
(0.03)	5 mils.

* Considerable deviations from these nominal values occurred in the case of individual coatings.

† 1 mil = 0.001 in.

The various combinations of metal or alloy coating, the method of application, and coating thickness will best be understood from Table II., in connection with which the following example explaining the method of reference should be noted :

The symbol (1.71) denotes a coating of metal (1), applied by method (0.7), and of *nominal* coating thickness (0.01); *i.e.*, a coating of aluminium, sprayed by the molten-metal pistol, and nominally 1 mil thick.

The basis specimens to which the coatings were applied consisted of mild-steel flats, $15 \times 10 \times \frac{3}{8}$ in., containing 0.20% of carbon, 0.60% of manganese, and 0.05% of silicon.

The exposure stations at which the tests were or are being carried out were as follows :

Home.	Atmospheric.	Overseas.	Marine.
Calshot		Apapa, Nigeria	Caernarvon
Llanwrtyd Wells		Congella, S. Africa	Gosport
Sheffield		Singapore ‡	

‡ These specimens have been lost.

In drawing up the experimental programme, special attention was paid to the protection of structural steelwork ; thus the specimens themselves are of ordinary mild steel and of the same size, $15 \times 10 \times \frac{3}{8}$ in., as those used in the tests of the main Committee (*see* Appendix A). The choice of the metallic coatings to be tested was governed by the same considerations. Nickel and copper coatings were omitted, because relatively thick and costly coatings would prove necessary to ensure adequate protection, as coatings of these metals may tend to increase the corrosion of steel by electrochemical action once they have been perforated.

The coatings under test include five metals,

zinc, aluminium, lead, tin, and cadmium, and two alloys, 88/12 lead-tin ("terne") and 82/18 cadmium-zinc (the eutectic composition). In all cases these coatings were applied by a variety of processes, viz., hot-dipping, cementation, electro-deposition, and spraying, in so far as each particular process was applicable to the metal or alloy concerned. A standard thickness of 3 mils was specified for the metallic coatings when practicable, but in many cases additional tests were made on thin (1 mil) and thick (5 mils) coatings. It should be noted that these figures are nominal and that the coatings as applied often showed wide variations from the specified figures. In all cases the weight of coating on each specimen was determined directly and in the following discussion the lives of the various coatings will be related to this figure rather than to the specified thickness.

The great majority of the metallic coatings were tested as they stood but, as detailed later, a few selected coatings (aluminium, lead, and zinc) were exposed to atmospheric corrosion after they had been given two coats of red oxide paint.

(b) *Examination of the Coated Specimens before Exposure.*

As detailed in Appendix B, the specimens were examined in the laboratory after coating and before exposure. Standard non-destructive methods were applied to all specimens, as appropriate, whilst a selected number of representative specimens of each type of coating was also examined by destructive methods. The latter work was undertaken by the British Non-Ferrous Metals Research Association.

(c) *Exposure of the Specimens.*

Sets of specimens have been exposed both to atmospheric corrosion (at six exposure stations) and to complete immersion in sea-water (at two exposure stations), as detailed below. Exposure was commenced at various times from July 1940 onwards, according to the station.

(i) *Atmospheric-Exposure Tests.*

Specimens were exposed to atmospheric-corrosion tests on six of the Committee's exposure sites as follows :

Sheffield.—A highly polluted industrial atmosphere.

Llanwrtyd Wells.—In central Wales, at a height of 1600 ft. The atmosphere is exceptionally free from industrial pollution, but the rainfall is heavy and the wind brings a certain amount of sea-salt in suspension.

Calshot.—A south-coast marine atmosphere, the exposure stands being on the beach. There is slight pollution by smoke from houses in the vicinity.

Congella (near Durban, South Africa).—A marine atmosphere.

Apapa (near Lagos, Nigeria).—A tropical marine atmosphere.

Singapore (Malay Peninsula).—A tropical marine atmosphere.

A summary of meteorological observations at these places is given in Table I., together with the dates of commencing exposure. Figures have been added for the rates of corrosion of (i) the Committee's standard mild steel X (0.2% C, 0.6% Mn, and 0.03% Cu) as determined for $15 \times 10 \times \frac{3}{8}$ -in. specimens over periods of 5 years, and

TABLE I.—*Particulars of the Atmospheric-Exposure Stations.*

Exposure Stations.	Approximate Position.		Average Meteorological Data.			Observed Rates of Corrosion, mils./year.			Date of Exposing Coated Specimens.
	Latitude.	Longitude.	Temperature, ° F.	Rainfall, in./year.	Relative Humidity, %.	Standard Mild Steel X. [*]	Ingot Iron.†	Pure Zinc.‡	
<i>Home.</i>									
Sheffield	53° N.	1° W.	48	30	84	4.21	4.95	0.64	16.7.40
Llanwrtyd Wells . .	52° N.	4° W.	47	55	79	1.24	2.37	0.12	6.8.40
Calshot	51° N.	1° W.	51	26	84	1.62	2.86	0.14	27.8.40
<i>Overseas.</i>									
Congella, S. Africa . .	30° S.	31° E.	71	43	76	1.84 §	3.27 §	0.16 §	8.4.42
Apapa, Nigeria . . .	7° N.	4° E.	80	72	79	0.77	1.09	0.04	20.3.41
Singapore, F.M.S. . .	2° N.	104° E.	81	95	80	0.58	0.62	0.04	3.4.41

* Results of 5-year tests on $15 \times 10 \times \frac{3}{8}$ -in. specimens exposed with mill scale.

† Results of 1-year tests on $4 \times 2 \times \frac{1}{8}$ -in. pickled specimens, changed annually. Mean value for the years during which the coated specimens have been exposed.

‡ Results of 1-year tests on $4 \times 2 \times \frac{1}{16}$ -in. specimens, changed annually. Mean value for the years during which the coated specimens have been exposed.

§ These results were obtained at a site used previously at Congella, about $\frac{3}{4}$ mile from the present site. The figures for ingot iron and zinc are the means of 9 observations.

|| Mean of 10 earlier observations.

(ii) small 4×2 -in. pollution specimens of ingot iron ($\frac{1}{8}$ in. thick) or zinc ($\frac{1}{16}$ in. thick). The latter figures refer to the average values for several sets of specimens, each exposed consecutively for periods of one year contemporaneously with the present tests. Considered as a whole, the data may be regarded as giving a good indication of the relative corrosiveness of the atmosphere at each testing station.

It would have been impracticable to expose complete sets of all the coatings tested at each exposure station. This was done at Sheffield only. Elsewhere smaller numbers of specimens, representing a selection of the various processes, were exposed. All tests were made in duplicate.

The method of exposure used in previous tests of the Corrosion Committee was employed, *i.e.*, the specimens were hung vertically, freely exposed, in two horizontal rows facing south. The upper and lower rows of specimens were approximately 4 ft. 6 in. and 2 ft. 6 in. from the ground, measuring to the lower edge. One duplicate of each pair of specimens was exposed in the upper, the other in the lower row. The four hooks used for suspending each specimen were made from $\frac{1}{4}$ -in. dia. steel wire, and were coated with the same metal used for coating the specimen, *e.g.*, all the specimens coated with cadmium were suspended by cadmium-plated hooks (*see* Fig. 1). This arrangement did not prove entirely satisfactory, as some of the hooks were inadequately protected and rusted after relatively short periods of exposure which led to rust streaks appearing on a few of the specimens. The rusted hooks have been replaced by hooks stove-enamelled over the metallic coating.

(ii) Sea-Water Immersion.

Tests on sets of specimens completely immersed in sea-water have been made at Caernarvon and at Gosport.

Most of the specimens exposed at Caernarvon were given coats of paint on top of the metallic coatings. They were immersed on steel frames below one of the Marine Corrosion Sub-Committee's rafts in July 1941. With a few exceptions, this test was concluded in July 1942, and the results obtained have already been published.¹

At Gosport the specimens were exposed under a floating landing stage; they were not painted before exposure. The specimens were carried vertically in two horizontal rows on steel frames fixed between the pontoons supporting the landing stage; they were secured to the frames by means of stainless-steel bolts and nuts passing through insulating sleeves and washers of laminated plastic material. The two rows of specimens were approximately 15 and 33 in. below the surface of the water. The duplicate specimens of each

protective scheme were arranged in different rows.

The Gosport tests were begun in April, 1941. The conditions of exposure rendered it impracticable to inspect the specimens in position at frequent intervals, so a few trial specimens were removed in October 1941, and April, 1942, as described elsewhere¹ (*loc. cit.*, p. 398 p). As a result it was decided to remove the remainder of the specimens in April 1943, after two years' immersion. The results of the observations then made will be described here. It was decided to continue the test on some of the zinc-coated specimens and these have since been re-immersed in a sea-water pool at Emsworth through the courtesy of Dr. I. G. Slater.

(d) Inspection of the Specimens and Final Examination.

(i) Field Inspections.

In general, the atmospheric specimens have been inspected after exposure periods of 1 month, 3 months, 6 months, 1 year, and thereafter at 6-monthly intervals. At the home stations all the routine inspections have been made by the same investigator, but local observers have kindly assisted in this respect overseas.

The observations included:

(1) Records of (a) blistering, (b) flaking, and (c) pitting.*

(2) Visual estimates of the percentage of the surface that was (a) discoloured, (b) rust-stained, or (c) rusted; the general distribution of the areas thus affected was also noted. Separate estimates were made for the front and back surfaces, but any breakdown obviously due to proximity to the edges or to the suspension hooks, or, in a few cases, to accidental mechanical damage, was ignored. Such damage and the breakdown arising therefrom was recorded.

(3) The condition of the edges, if different from that of the main surfaces, was recorded separately.

The method may be illustrated by the following typical report on two specimens.

Specimen A.

Front.—20% rust stain and 5% rust on spray lines.

Back.—5% rust stain and 2% rust on spray lines.

Edges.—40% rusted, mostly on top edge.

Specimen B.

Front.—60% white deposit, 1% rust in small spots mainly near left edge.

Back.—80% white deposit, 5% rust in small spots mainly near right edge, 2% blistering near left edge.

Edges.—Intact.

These reports are entered on standard forms, enabling the progress of the corrosion of each

* So far, no pitting of specimens exposed to the atmosphere has been observed.

specimen to be followed. In addition, to facilitate comparison of different coatings, the front and back faces of each specimen are graded in the following categories, on the basis of the data recorded as above :

- x* Excellent. No sign of breakdown of the coating.
- f* Fair. Coating showing signs of breakdown, *e.g.*, blistered, discoloured, or rust-stained to any extent, or the underlying steel rusted over less than 5% of the area. A metallic coating followed by paint is regarded as a single composite coating; hence grade "fair" is reached when the paint first shows signs of breakdown.
- o* Failed. 5% or more of the steel rusted.

The life of the protective scheme on each specimen is deduced from the gradings made at successive inspections. Two figures are computed which correspond, respectively, to the life until the first signs of breakdown and to the life until failure (5% rust); again separate estimates are made for the front and back surfaces.

As already stated, routine inspection of the specimens immersed in the sea at Gosport was impracticable. At the completion of the 2 years' test, the specimens were scraped free from marine growths, washed, and returned to the laboratory for final examination.

(ii) *Final Laboratory Examination.*

In the case of the atmospheric-exposure tests at home stations, specimens graded as failed (5% or more rust) on both the front and back surfaces at two or more consecutive inspections are removed at convenient intervals. After return to the laboratory, they are washed and weighed. Then the coatings are examined in detail, estimates of the percentage of the surface rusted, &c., being made as in the field inspections.

Attempts have been made to determine the coating thickness after exposure, using an electromagnetic layer thickness meter as described in Appendix B, but the values obtained bear no relation to the original coating thickness. This is not due to any fault in the meter, but probably to the fact that the specimens are partly rusted, and the meter does not indicate the true residual coating thickness when the steel surface is covered with a mixture of the coating metal, its corrosion product, and rust. For the same reason, the change in weight of the specimens after exposure has not proved to be of great significance. It has not been considered necessary to attempt to devise a method of removing the rust and the corrosion product of the coating metal; furthermore, in view of the necessity of avoiding any attack on the steel base or the remaining coating metal, this would prove to be a difficult matter in many cases.

The specimens immersed in sea-water were examined in the same way as the atmospheric

specimens. On some of the specimens the steel base was appreciably pitted; the depths of the pits were measured with a spherometer and their diameters were noted.

4.—RESULTS.

The results of the tests to date are given in Tables II., III., and IV., which refer, respectively, to the atmospheric tests on metallic coatings, the atmospheric tests on metallic coatings exposed in the painted condition, and the total-immersion tests in sea-water at Gosport.

In the case of the atmospheric-exposure tests (Tables II. and III.), the results are classified under each exposure station and the following data are given where appropriate :

- W* Weight of coating, g./specimen.
- T_m* Coating thickness, mils. Average value obtained by the electromagnetic meter (*see* Appendix B).
- L_f* Life of coating to grade "fair," years. Mean value for the front and back surfaces.
- L_o* Life of coating to grade "failed," years. Mean value for the front and back surfaces.

The values of *L_f* and *L_o* are based on the inspections made during exposure as previously described (*see* section 3, (d), (i)). Laboratory examination of specimens removed after failure confirmed the field inspections; as already stated, the change in weight and the change in coating thickness (measured by the electromagnetic meter) were of no significance and are not given here.

The results for the sea-water immersion tests (given in Table IV.) are based on laboratory examination after 2 years' immersion, as inspection of the specimens *in situ* was not practicable. The specimens were cleaned roughly with a wooden scraper at the site, returned to the laboratory, and brushed in fresh running-water before examination.

5.—DISCUSSION OF THE RESULTS OF THE ATMOSPHERIC-CORROSION TESTS.

(a) *Introduction.*

As already mentioned, a complete set of specimens was exposed to atmospheric corrosion at Sheffield only. This set included the thinnest metallic coatings tested, nominally 1 mil thick, whereas, as a general rule, only metallic coatings of medium thickness, nominally 3 mils, were exposed at the other five atmospheric-corrosion stations. This fact, together with the greater corrosiveness of the Sheffield atmosphere for most metals, has led to the position revealed by Table II., *viz.*, that most of the coating failures to date have occurred at Sheffield. Accordingly, it should be understood that the remarks made in the following discussion refer in the main to the results obtained at Sheffield under conditions of exposure

TABLE II.—*Results of the Atmospheric-Exposure Tests on Metallic Coatings.*

A list of symbols is given at the beginning of section (3).

Values of W have been rounded off to the nearest gramme and those of L_f and L_0 to 0.1 year.

Coating.		Exposure Stations.											
Reference No. and Process.		Sheffield.				Llanwrtyd Wells.				Calshot.			
		W.	T _m .	L _f .	L _o .	W.	T _m .	L _f .	L _o .	W.	T _m .	L _f .	L _o .
(1) <i>Aluminium Coatings.</i>													
(1.02) Cemented or calorized.		36 42	6.4 7.6	0.0 0.0	1.5 2.5	35 33	6.1 7.8	0.1 0.1	0.1 0.1	43 44	7.8 8.2	0.1 0.1	0.1 0.6
(1.42) Hot-dipped.		141 139	14.5 15.7	0.0 0.0	> 5.0 > 4.0	136 123	13.0 11.4	0.1 0.1	1.0 1.0	139 136	14.5 13.9	0.1 0.1	> 5.2 1.6
(1.62) Hot-dipped and heat-treated.		139 125	17.1 19.4	0.0 0.0	3.3 2.5	143 152	17.4 19.0	0.1 0.1	0.3 0.3	146 147	17.7 18.3	0.1 0.1	0.1 3.0
(1.71) Sprayed by molten-metal pistol.		18 14	2.7 2.2	0.1 0.0	2.0 1.6
(1.72) " " " "		24 16	3.3 2.2	0.1 0.0	> 3.8 2.3	31 28	4.5 3.4	0.1 0.2	> 3.8 > 4.9	24 18	3.3 2.4	0.2 0.1	> 5.2 1.5
(1.73) " " " "		85 73	11.0 12.1	4.0 4.3	> 5.0 > 5.0
(1.81) Sprayed by powder pistol.		24 17	3.0 2.1	0.3 0.0	2.3 2.3
(1.82) " " " "		40 39	4.3 4.3	0.3 0.1	2.5 > 3.8	47 51	5.5 5.6	0.1 0.1	0.6 0.6	32 29	3.9 3.5	0.1 0.1	2.1 > 5.2
(1.83) " " " "		89 114	10.7 12.9	0.4 1.0	2.3 2.1
(1.91) Sprayed by wire pistol.		18 21	2.4 2.8	0.2 0.3	2.5 2.5
(1.92) " " " "		47 44	4.7 4.5	4.0 4.0	> 5.0 > 5.0	45 53	4.5 5.9	4.9 4.8	> 4.9 > 4.9	42 44	4.2 4.5	4.6 5.2	> 5.2 > 5.2
" " " "		48 43	4.7 4.4	4.0 4.0	> 5.0 > 5.0
" " " "		46 40	4.8 4.1	4.0 4.0	> 5.0 > 5.0
(1.93) " " " "		71 60	7.2 6.6	3.8 4.0	> 5.0 > 5.0
(2) <i>Cadmium Coatings.</i>													
(2.21) Electrodeposited, cyanide bath.		45 46	1.7 2.0	0.7 0.7	1.6 1.0	44 45	1.8 1.8	4.8 > 4.9	> 4.9 > 4.9
(2.22) " " " "		129 145	3.3 3.7	1.6 2.0	1.3 3.0	126 131	3.4 3.6	> 4.9 > 4.9	> 4.9 > 4.9	139 132	3.6 3.5	> 5.2 2.5	> 5.2 > 5.2
(2.23) " " " "		222 216	5.0 4.8	4.3 2.3	4.5 4.0
(2.32) Electrodeposited, cyanide bath and chromate rinsed.		135 136	3.3 3.4	2.3 2.0	2.5 2.5
(2.71) Sprayed by molten-metal pistol.		54 61	2.2 2.3	0.2 0.1	1.0 1.0
(2.72) " " " "		83 81	2.7 2.4	0.7 0.5	1.3 1.3	53 84	2.1 2.7	0.1 1.8	> 4.9 > 4.9	77 77	2.7 2.5	1.0 0.5	> 5.2 > 5.2
(2.73) " " " "		139 93	3.7 2.9	1.0 0.4	2.0 1.6
(2.82) Sprayed by powder pistol.		141 132	4.1 3.8	2.1 1.6	2.8 2.8	132 58	3.9 2.4	> 4.9 > 4.9	> 4.9 > 4.9
(2.92) Sprayed by wire pistol.		86 97	2.9 2.7	0.7 0.4	1.8 1.8
(3) <i>Cadmium-Zinc (82/18) Alloy Coatings.</i>													
(3.71) Sprayed by molten-metal pistol.		28 28 66 71 85 133	1.4 1.4 2.5 2.6 2.9 4.1	0.2 0.3 0.4 0.6 1.0 1.0	1.0 1.0 1.6 1.3 1.6 1.6
(3.72) " " " "		66 71	2.5 2.6	0.4 0.6	1.6 1.3	38 40	1.7 1.7	4.1 > 4.8	> 4.9 > 4.9	63 60	2.4 2.5	> 5.2 2.8	> 5.2 4.6
(3.73) " " " "		85 133	2.9 4.1	1.0 1.0	1.6 1.6
(3.82) Sprayed by powder pistol.		61 59	2.5 2.6	1.0 0.9	1.6 1.5	58 71	2.5 2.8	> 4.9 > 4.9	> 4.9 > 4.9
(4) <i>Zinc Coatings.</i>													
(4.01) Cemented (sherardized).		40 30 34 32	1.4 1.2 1.3 1.2	1.0 0.5 0.7 0.5	2.5 2.0 2.1 2.3	36 36 29 34	1.3 1.2 1.1 1.2	2.0 2.0 1.0 2.0	> 4.9 > 4.9 > 4.9 > 4.9	30 32 ...	1.1 1.2 ...	3.0 3.3 ...	> 5.2 > 5.2 ...
(4.12) Electrodeposited, sulphate bath.		111 111	3.0 3.1	> 4.8 > 4.8	> 5.0 > 5.0	109 108	2.8 2.9	> 4.9 > 4.4	> 4.9 > 4.9	104 110	2.8 2.9	> 5.2 > 5.2	> 5.2 > 5.2
(4.21) Electrodeposited, cyanide bath.		37 33	1.1 1.0	1.8 1.6	2.3 1.6	39 36	1.2 1.1	> 4.9 > 4.9	> 4.9 > 4.9	37 37	1.1 1.1	> 5.2 > 5.2	> 5.2 > 5.2
(4.22) " " " "		109 108	3.1 2.9	> 5.0 4.6	> 5.0 > 5.0	111 115	3.0 3.2	> 4.9 > 4.9	> 4.9 > 4.9	112 111	2.8 2.9	> 5.2 > 5.2	> 5.2 > 5.2
(4.23) " " " "		180 182	4.4 4.7	> 5.0 > 5.0	> 5.0 > 5.0
(4.32) Electrodeposited, cyanide bath and chromate rinsed.		113 113	3.0 5.0	> 5.0 > 5.0	> 5.0 > 5.0

TABLE II.—*Continued.*A list of symbols is given at the beginning of section (3). Values of W have been rounded off to the nearest gramme and those of L_f and L_o to 0.1 year.

Coating.	Exposure Stations.											
Reference No. and Process.	Sheffield.				Llanwrtyd Wells.				Calshot.			
	W.	T _m .	L _f .	L _o .	W.	T _m .	L _f .	L _o .	W.	T _m .	L _f .	L _o .
(4) Zinc Coatings—Continued.												
(4.41) Hot-dipped (Firm A).	68	1.9	1.0	3.0	63	2.2	>4.4	>4.9	64	2.0	>5.2	>5.2
	59	1.8	0.6	3.0	65	2.2	3.9	>4.9	71	2.1	>5.2	>5.2
(4.42) " "	90	2.8	0.3	4.5	99	2.8	>4.9	>4.9	97	2.8	>5.2	>5.2
	93	2.8	1.6	5.0	90	2.8	>4.9	>4.9	92	2.8	>5.2	>5.2
(4.43) " "	166	4.7	3.0	>5.0
	150	4.2	3.0	>5.0
(4.52) Hot-dipped (Firm B).	123	3.5	2.0	>5.0	124	3.6	>4.9	>4.9	91	2.7	>5.2	>5.2
	96	2.7	1.6	5.0	113	3.1	4.9	>4.9	154	4.3	>5.2	>5.2
(4.71) Sprayed by molten-metal pistol.	27	1.1	Lost.	
	27	1.2	0.6	1.6
(4.72) " " " "	57	2.0	2.0	3.0	63	2.2	>4.9	>4.9	57	2.1	4.3	>5.2
	46	1.8	2.1	2.3	66	2.1	>4.9	>4.9	62	2.4	3.5	>5.2
(4.73) " " " "	109	3.6	4.0	5.0
	117	3.8	3.0	>4.2
(4.81) Sprayed by powder pistol.	61	2.2	2.3	2.8
	57	2.3	2.0	2.8
(4.82) " " " "	151	4.8	>5.0	>5.0	179	6.1	>4.9	>4.9	154	5.2	>5.2	>5.2
	139	4.8	>5.0	>5.0	196	6.0	>4.9	>4.9	138	4.7	>5.2	>5.2
(4.83) " " " "	265	8.6	>5.0	>5.0
	250	8.2	>5.0	>5.0
(4.91) Sprayed by wire pistol.	35	1.3	1.3	1.8	31	1.2	>4.9	>4.9
	32	1.2	0.9	1.8	27	1.1	>4.9	>4.9
(4.92) " " " "	89	2.8	3.5	4.0	100	3.5	>4.9	>4.9	91	3.0	>5.2	>5.2
	79	2.7	2.5	3.5	102	3.2	>4.9	>4.9	111	3.8	>5.2	>5.2
" " " "	72	2.5	2.5	3.3	98	3.2	>5.2	>5.2
	81	3.0	3.0	3.8	100	3.4	>5.2	>5.2
(4.93) " " " "	128	4.2	4.6	>5.0
	142	4.2	>5.0	>5.0
(5) Lead Coatings.												
(5.11) Electrodeposited, perchlorate bath.	61	1.0	0.2	>5.0	61	0.9	0.1	1.6
	63	1.1	0.1	>5.0	59	1.0	0.1	1.0
(5.12) " " " "	186	2.4	>5.0	>5.0	182	2.4	0.2	>4.4	185	2.4	0.5	>4.1
	185	2.5	>5.0	>5.0	182	2.5	1.4	>4.9	203	2.6	0.5	>5.2
(5.13) " " " "	310	4.2	>5.0	>5.0
	300	4.1	>5.0	>5.0
(5.41) Hot-dipped.	43	0.6	0.1	>5.0	34	0.6	0.1	0.6	47	0.6	0.1	1.0
	44	0.7	0.3	>5.0	43	0.7	0.1	0.6	40	0.6	0.1	1.5
(5.71) Sprayed by molten-metal pistol.	140	1.8	0.2	>5.0
	135	2.0	0.0	>5.0
(5.72) " " " "	254	3.6	>5.0	>5.0	184	2.9	0.2	>4.9	162	2.4	0.2	1.5
	210	3.0	0.1	>5.0	182	2.5	0.3	>4.9	220	3.2	0.2	>5.2
(5.73) " " " "	257	4.0	>5.0	>5.0
	98	2.0	0.0	>5.0
(5.82) Sprayed by powder pistol.	68	1.4	0.3	>4.2	179	3.1	0.2	>4.9	58	1.2	0.1	1.0
	71	1.4	0.5	>4.8	140	2.5	0.3	>4.9	66	1.3	0.1	1.5
(5.92) Sprayed by wire pistol.	259	4.8	>5.0	>5.0	240	4.7	0.6	>3.8	300	5.6	0.6	>5.2
	243	4.2	>5.0	>5.0	242	4.1	1.0	>4.9	245	4.3	>5.2	>5.2
(6) Lead-Tin (88/12) Alloy Coatings.												
(6.41) Hot-dipped.	26	0.6	0.0	>4.8	27	0.5	0.1	1.0
	28	0.6	0.1	>5.0	27	0.5	0.1	1.0
(6.71) Sprayed by molten-metal pistol.	88	1.8	0.0	4.5
	92	1.8	0.0	>4.5
(6.72) " " " "	158	3.0	0.0	>5.0	178	3.2	0.1	1.6	110	1.6	0.1	1.0
	145	2.7	0.0	>5.0	135	2.3	0.1	1.0	159	2.7	0.1	1.5
(6.73) " " " "	132	2.6	0.0	>5.0
	137	2.7	0.0	>5.0
(6.82) Sprayed by powder pistol.	252	4.9	0.2	>5.0
	254	5.0	0.5	>5.0
(7) Tin Coatings.												
(7.22) Electrodeposited, stannate bath.	117	3.1	>5.0	>5.0	119	2.7	0.3	3.6	105	2.6	0.4	1.5
	111	2.9	>5.0	>5.0	115	2.7	0.3	2.8	86	1.5	0.3	1.5
(7.41) Hot-dipped.	22	0.6	0.6	>5.0
	22	0.5	1.0	>5.0
(7.71) Sprayed by molten-metal pistol.	33	1.1	0.0	1.6
	43	1.4	0.0	1.6
(7.72) " " " "	38	1.3	0.0	2.3	48	1.5	0.1	0.6	39	1.2	0.1	0.4
	50	1.3	0.0	3.5	56	1.5	0.1	0.6	73	2.1	0.1	1.0
(7.73) " " " "	106	2.9	0.0	>4.2
	98	2.9	0.0	>4.0
(7.82) Sprayed by powder pistol.	136	4.1	0.0	3.0	181	5.1	0.1	0.8
	153	4.3	0.0	3.0	123	3.5	0.1	0.8

A list of symbols is given at the beginning of section (3). Values of W have been rounded off to the nearest gramme and those of L_0 and L_f to 0.1 year.

[illegible]

TABLE II.—*Continued.*A list of symbols is given at the beginning of section (3). Values of W have been rounded off to the nearest gramme and those of L_0 and L_f to 0.1 year.

Coating.	Exposure Stations.											
	Congella, S. Africa.				Apapa, Nigeria.				Singapore.			
	W .	T_m .	L_f .	L_0 .	W .	T_m .	L_f .	L_0 .	W .	T_m .	L_f .	L_0 .
(4) <i>Zinc Coatings</i> —Continued.												
(4.41) Hot-dipped (Firm A).	59	1.8	> 0.5	> 0.5
	62	1.9	> 0.5	> 0.5
(4.42) " "	85	2.6	> 3.0	> 3.0	90	2.8	> 4.0	> 4.0	88	2.6	> 0.5	> 0.5
	88	2.7	> 3.0	> 3.0	92	2.7	> 4.0	> 4.0	89	2.6	> 0.5	> 0.5
(4.43) " "
(4.52) Hot-dipped (Firm B).
(4.71) Sprayed by molten-metal pistol.
(4.72) " " " "	66	2.2	> 3.0	> 3.0
	78	2.8	> 3.0	> 3.0
(4.73) " " " "
(4.81) Sprayed by powder pistol.
(4.82) " " " "	203	6.7	> 3.0	> 3.0	208	7.0	> 0.5	> 0.5
	181	6.2	> 3.0	> 3.0	200	6.8	> 0.5	> 0.5
(4.83) " " " "
(4.91) Sprayed by wire pistol.
(4.92) " " " "	112	3.4	> 3.0	> 3.0	91	2.9	> 4.0	> 4.0
	105	3.2	> 3.0	> 3.0	98	2.9	> 4.0	> 4.0
" " " "
(4.93) " " " "
(5) <i>Lead Coatings</i> .												
(5.11) Electrodeposited, perchlorate bath.
(5.12) " " " "	178	2.3	> 0.5	> 0.5
	182	2.2	> 0.5	> 0.5
(5.13) " " " "
(5.41) Hot-dipped.
(5.71) Sprayed by molten-metal pistol.
(5.72) " " " "	192	3.0	0.3	0.3
	228	3.8	0.3	> 3.0
(5.73) " " " "
(5.82) Sprayed by powder pistol.	141	2.5	0.5	> 0.5
	134	2.4	0.5	> 0.5
(5.92) Sprayed by wire pistol.	270	4.7	2.3	> 4.0
	208	3.8	0.4	> 4.0
(6) <i>Lead-Tin (88/12) Alloy Coatings</i> .												
(6.41) Hot-dipped.	23	0.4	0.1	> 4.0
	24	0.5	0.0	> 4.0
(6.71) Sprayed by molten-metal pistol.
(6.72) " " " "	187	2.6	0.3	1.0
	117	2.2	0.3	> 2.1
(6.73) " " " "
(6.82) Sprayed by powder pistol.	190	3.8	0.3	> 0.5
	187	3.7	0.0	0.5
(7) <i>Tin Coatings</i> .												
(7.22) Electrodeposited, stannate bath.
(7.41) Hot-dipped.
(7.71) Sprayed by molten-metal pistol.
(7.72) " " " "	65	1.7	0.3	0.3
	57	2.1	0.3	1.6
(7.73) " " " "
(7.82) Sprayed by powder pistol.	178	5.0	0.3	> 0.5
	168	4.8	0.1	> 0.5

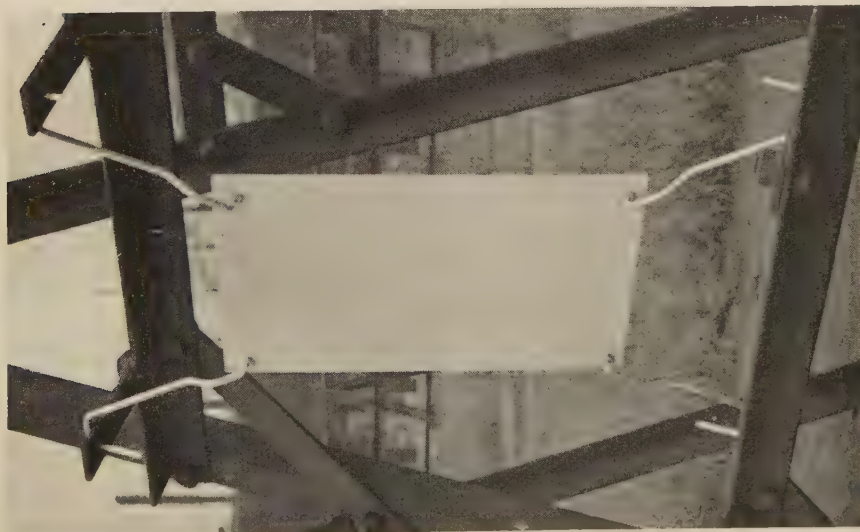


FIG. 1.—Method of Suspending Specimens for Atmospheric-Corrosion Tests.



FIG. 2.—5.0 Years at Sheffield. Aluminium (1.92) sprayed by wire pistol. Coating weight, 48 g. (0.8 oz. sq. ft.). Blistering, 5%. Grade *f*. (Part of specimen. Reduced to nine-tenths linear in reproduction.)



FIG. 3.—1.6 Years at Sheffield. Aluminium (1.83) sprayed by powder pistol. Coating weight, 89 g. (1.4 oz. sq. ft.). Blistering, 95%; flaking, 20%; rusting, 10%. Grade *o*. (Full front surface of a 15 × 10-in. specimen, reduced to three-tenths linear.)



FIG. 4.—40 Years at Sheffield. Zinc (4.42) hot-dipped. Coating weight, 90 g. (1.4 oz./sq. ft.). Discoloured, 95%; rusted, 5%. Grade o.

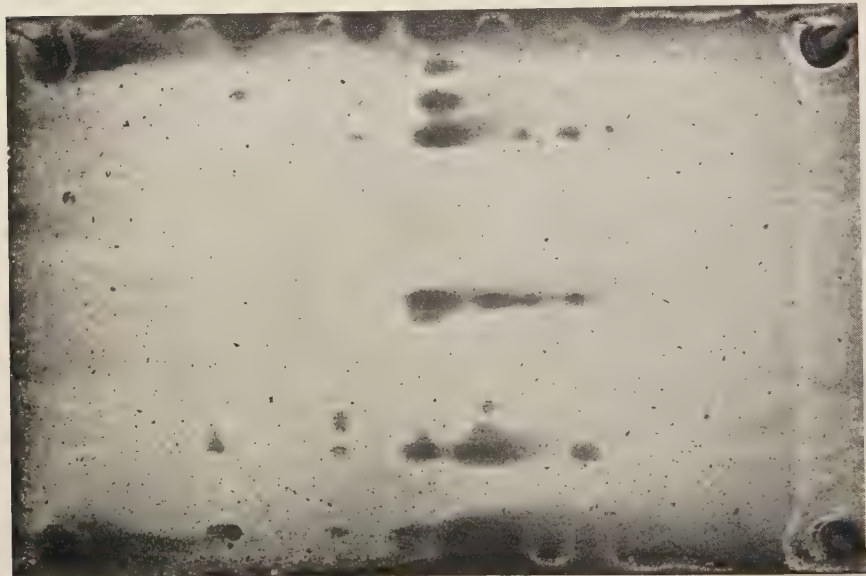


FIG. 5.—40 Years at Sheffield. Zinc (4.92) sprayed by wire pistol. Coating weight, 89 g. (1.4 oz./sq. ft.). Rusted, 5% on spray lines. Grade o.



FIG. 6.—40 Years at Sheffield. Zinc (4.22) electrodeposited (cyanide bath). Coating weight, 108 g. (1.7 oz./sq. ft.). Intact. Grade x. (The black spots are surface dirt.)

Full front surfaces of 15 × 10-in. specimens, reduced to three-tenths linear).

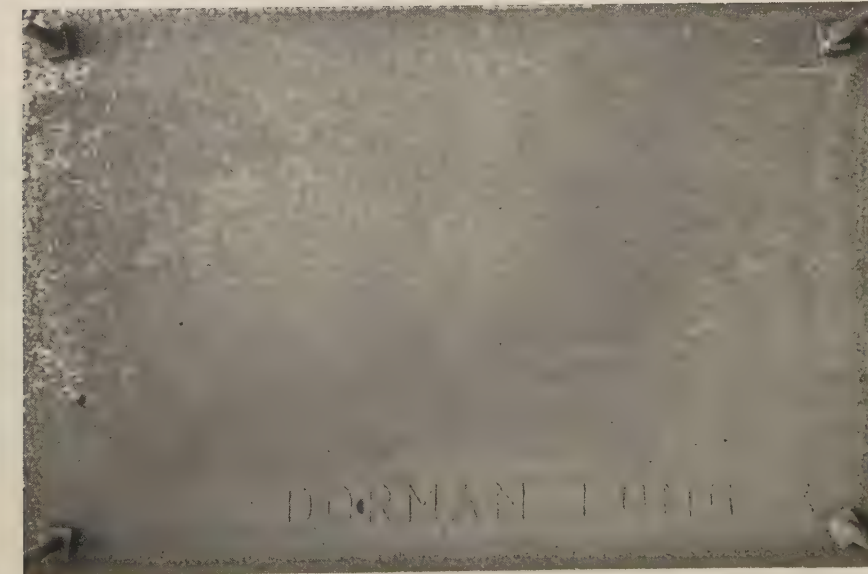


FIG. 7.—40 Years at Sheffield. Lead (5.41) hot-dipped. Coating weight, 44 g. (0.7 oz./sq. ft.). Discoloured, 70%; rusted, 1% (in small spots). Grade f.



FIG. 8.—22 Years at Calshot. Lead (5.41) hot-dipped. Coating weight, 47 g. (0.7 oz./sq. ft.). Rusted, 50%. Grade o.

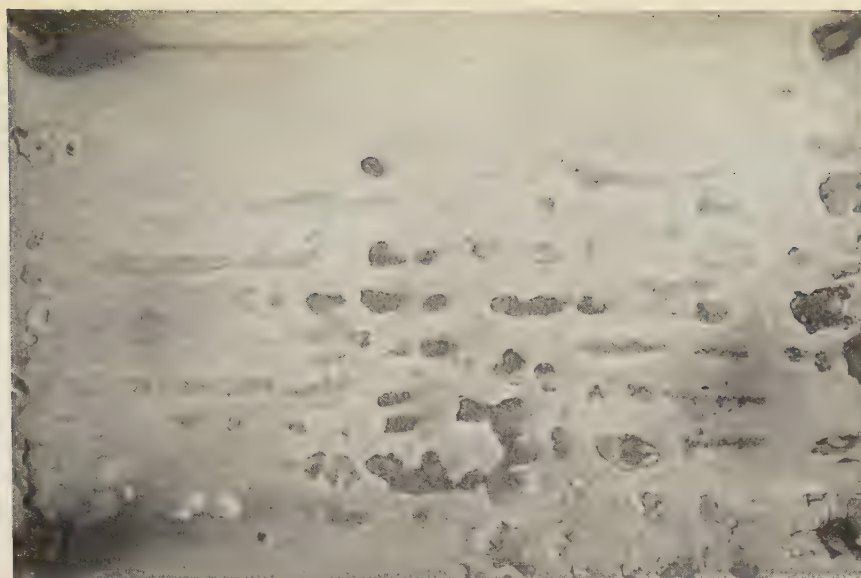


FIG. 9.—26 Years at Llanwrtyd Wells. Lead (5.92) sprayed by wire pistol. Coating weight, 240 g. (3.8 oz./sq. ft.). Flaking, 5%; rusted, 5%. Grade o.

(Full front surfaces of 15 × 10-in. specimens, reduced to three-tenths linear).

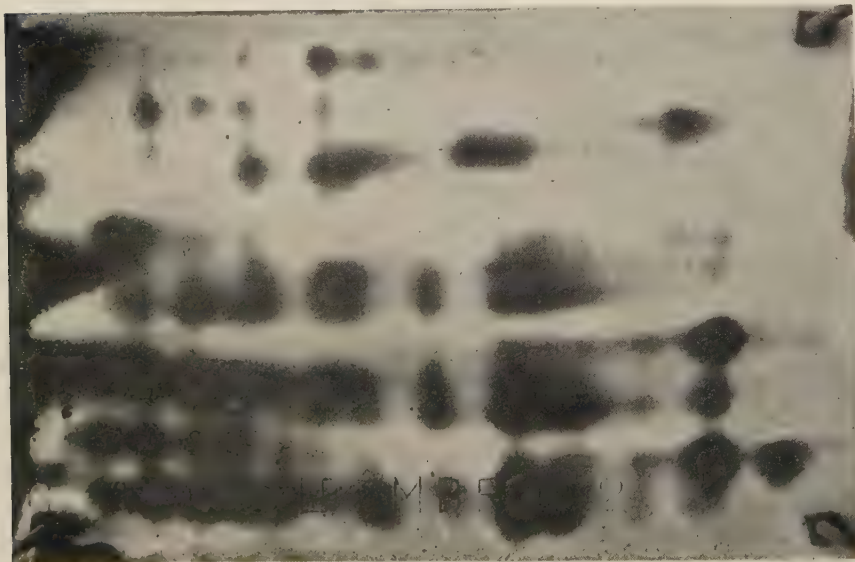


FIG. 10.—1.6 Years at Sheffield. Cadmium (2.73) sprayed by molten-metal pistol. Coating weight, 93 g. (1.5 oz. sq. ft.). Rusted 20% on spray lines. Grade o.



FIG. 11.—2.6 Years at Llanwrtyd Wells. Tin (7.12) electro-deposited (stannate bath). Coating weight, 115 g. (1.8 oz. sq. ft.). Rusted, 15% (mainly near bottom left corner and in spots). Grade o.

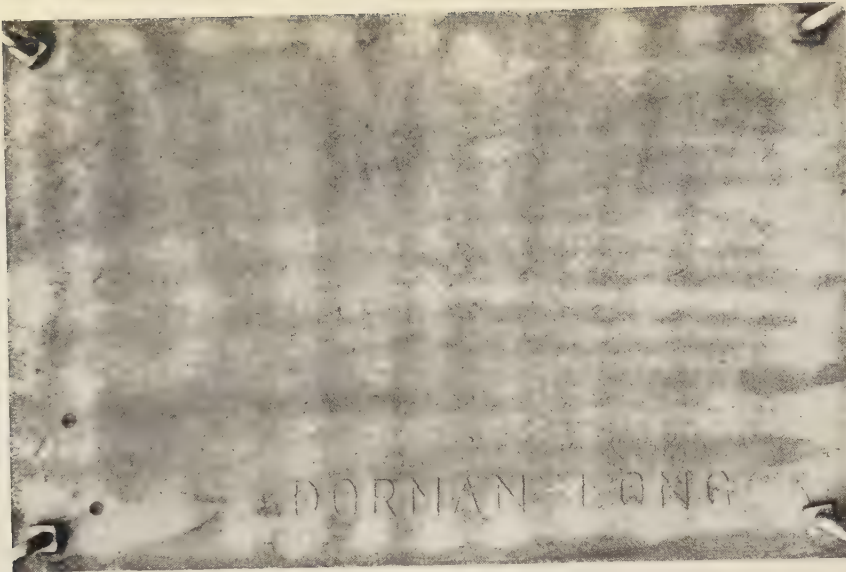


FIG. 12.—28 Days at Sheffield. Tin (7.73) sprayed by molten-metal pistol. Coating weight, 106 g. (1.7 oz. sq. ft.). Rust-staining 20% (on spray lines). Grade f.

(Full front surfaces of 15 × 10-in. specimens, reduced to three-tenths linear.)

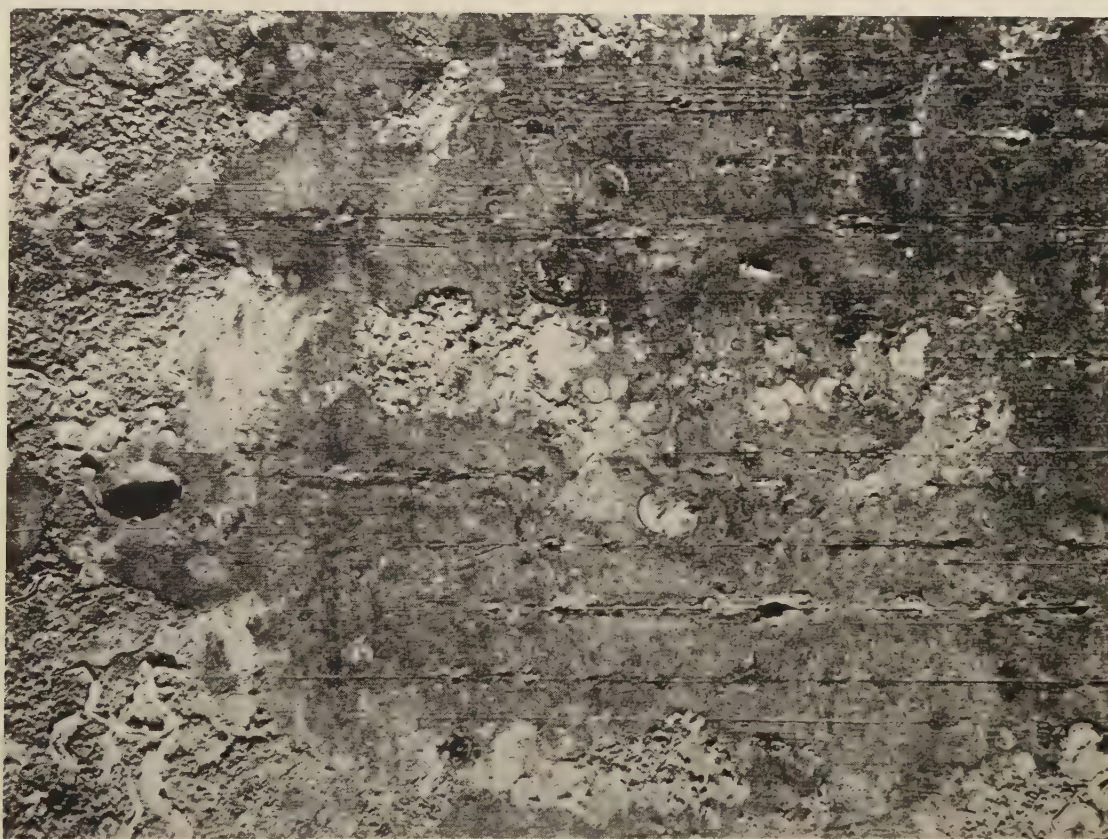


FIG. 13.—2 Years in Sea-Water at Gosport. Lead (5-13) electrodeposited (perchlorate bath). Coating weight, 311 g. (4.9 oz./sq. ft.). Rusted, 5% (mainly on original rolling scratches). Grade J. Maximum pit depth, 6 mm. (Part of specimen, natural size.)

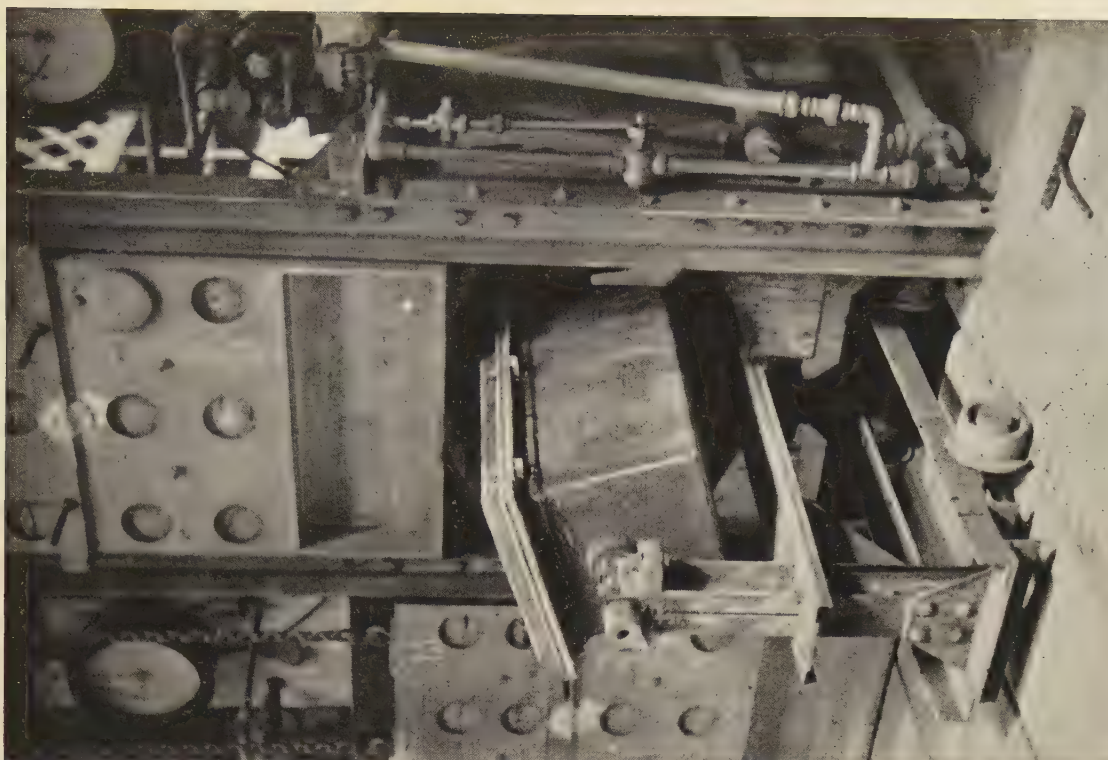


FIG. 14.—Preparation of Cemented Zinc (Sherardized) Coatings, showing drum containing specimens, zinc-dust, and sand, being placed in a gas-fired furnace.



FIG. 15.—Preparation of Hot-Dipped Zinc Coatings (Firm B).

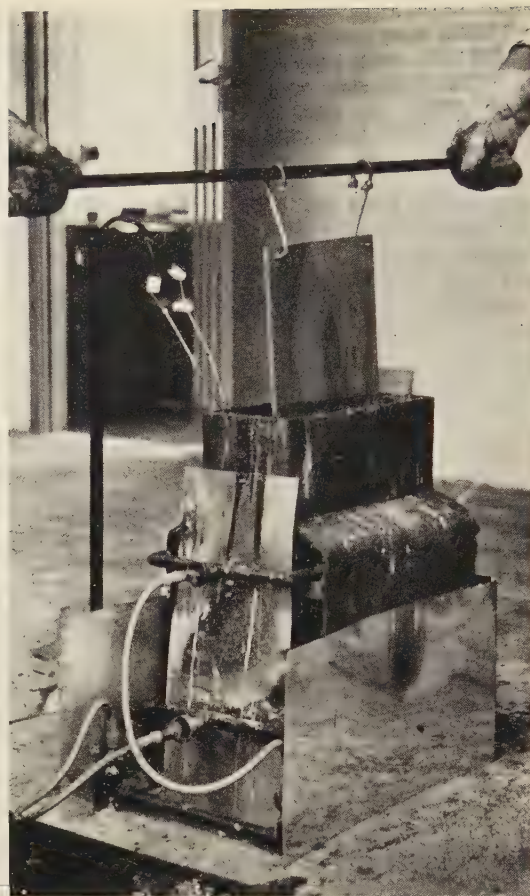


FIG. 16.—Preparation of Hot-Dipped Tin Coatings.

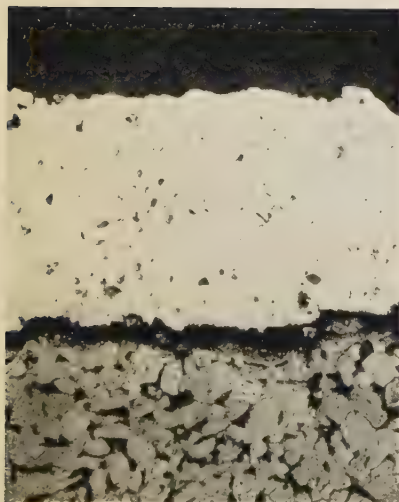


FIG. 17.—Aluminium (1.83), Sprayed by the Power Pistol.

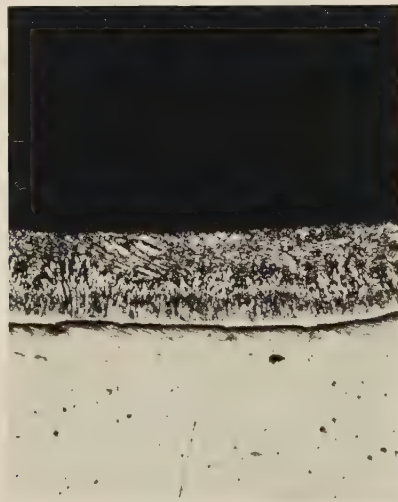


FIG. 18.—Zinc (4.43), Hot-Dipped.

FIGS. 17, 18, and 19.—Unetched. $\times 150$.

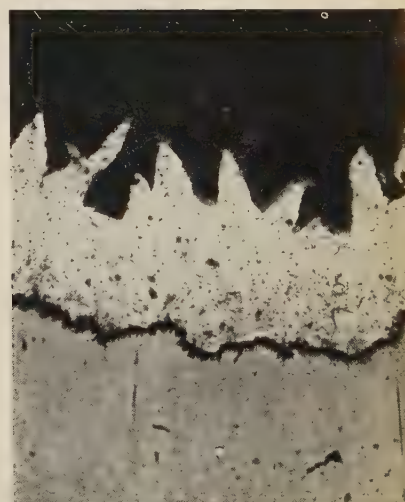


FIG. 19.—Cadmium (2.22), Electrodeposited (Cyanide Bath). (See text.)

(Figs. 17 to 19 reduced to seven-eighths linear in reproduction.)

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TABLE III.—Results of the Atmospheric-Exposure Tests on Metallic Coatings Painted with Red Oxide Paint (2 Coats).

Coating Process.	Exposure Stations.															
	Sheffield.				Llanwrtyd Wells.				Calshot.				Singapore.			
	W.*		L _f .	L _o .	W.*		L _f .	L _o .	W.*		L _f .	L _o .	W.*		L _f .	L _o .
	(a).	(b).			(a).	(b).			(a).	(b).			(a).	(b).		
Two coats of red oxide paint over the following metallic coatings : (1.02) Aluminium, cemented.	47 43	50 49	5.0 5.0	>5.0 >5.0	35 39	44 50	3.1 3.1	>4.9 >4.9
(1.91) Aluminium, sprayed by the wire pistol.	17	26	5.0	>5.0
(1.92) " " " "	18 46 52	27 26 26	5.0 5.0 5.0	>5.0 >5.0 >5.0
(4.01) Zinc, cemented.	44 29	21 22	2.5 3.3	>5.0 >5.0	28 43	21 20	2.0 2.0	>4.9 >4.9	33 43	21 21	1.3 1.0	>5.2 >5.2	27 43	21 22	>0.5 >0.5	>0.5 >0.5
(4.41) Zinc, hot-dipped.	62	20	2.5	>4.0
(4.42) " "	65 90 93	20 20 19	3.0 2.5 3.0	>5.0 >5.0 >5.0
(4.91) Zinc, sprayed by the wire pistol.	30 32	25 23	2.3 4.0	>5.0 >5.0
(4.92) " " " "	95 96	26 25	4.0 4.0	>5.0 >5.0	110 86	27 26	3.3 2.5	>4.9 >4.9
(5.11) Lead, electrodeposited.	62 62	20 20	5.0 >5.0	>5.0 >5.0
(5.12) " "	186 183	22 20	>5.0 5.0	>5.0 >5.0	182 184	21 21	>4.8 >4.9	>4.9 >4.9
... Bare steel.†	21 22	3.0 3.0	>5.0 >5.0	23 22	1.5 1.4	>4.9 >4.9	22 21	1.6 1.0	>5.2 >5.2	22 21	>0.5 >0.5	>0.5 >0.5

* W = weight of coating, g./specimen (a) of the metallic coating, and (b) of the dry paint film. Values of W have been rounded off to the nearest gramme, and those of L_f and L_o to 0.1 year.

† Control specimens pickled by the sulphuric-acid/phosphoric-acid process.

to an industrial atmosphere, although references to results at the other stations will be made as appropriate. It should further be stressed that this is an interim statement based on observations up to a maximum period of about 5 years' exposure.

(b) Aluminium Coatings.

The lives until failure (L_o) of the aluminium coatings exposed at Sheffield are plotted against the weights of coating (W) in Fig. 20. It will be seen that the method of application has had a considerable influence on the results. In particular, it may be noted that, apart from a single hot-dipped specimen with the heaviest coating weight, the only coatings that have not failed after 5 years' exposure are those sprayed by the wire pistol or by the molten-metal pistol, and having a coating weight exceeding 40 g./specimen (0.6 oz./sq. ft.).

Cemented Coatings.—These showed rust stains shortly after exposure and have now failed.

Hot-Dipped Coatings.—These also became stained quickly, but breakdown beyond this stage spread slowly at Sheffield and the specimens do not yet show 5% of the steel rusted. At Llanwrtyd Wells failure occurred more rapidly and at the other stations erratic results were obtained. Heat-treatment of the hot-dipped coatings re-

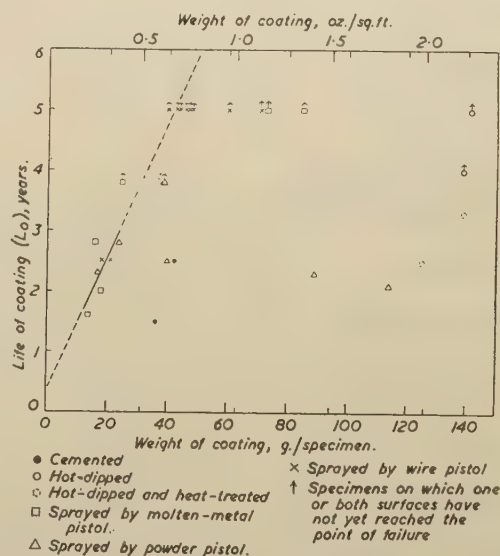


FIG. 20.—Lives of Aluminium Coatings Exposed at Sheffield.

duced the protection afforded. On the whole, these cemented or hot-dipped aluminium coatings cannot be regarded as satisfactory for protection against atmospheric corrosion under these conditions but, as is pointed out in Appendix A, it

TABLE IV.—Results of the Total-Immersion Tests in Sea-Water at Gosport.

Coating.			Examination after 2 Years' Immersion.								
Reference No. and Process.	Weight (W), g./specimen.	Thickness* (T_m), mils.	Change in Weight,† g.	Grade.‡	Surface Area Rusted,§ %.		Pitting.		Fouling.**		Notes.
					Front.	Back.	Front.	Back.	Barnacles.	Tube-worms.	
(1) <i>Aluminium Coatings.</i>											
(1.42) Hot-dipped.	129 130	11.6 10.8	— 41 13	<i>o</i> <i>o</i>	98 30	60 30	<i>b</i> <i>b</i>	<i>w</i>
(1.73) Sprayed by the molten-metal pistol.	67 54	9.7 7.3	9 11	<i>x</i> <i>f</i>	0 0.05	0 0.1	<i>b</i> <i>b</i>	<i>w</i> <i>w</i>	0.2% medium pits in the coating on the back surface.
(1.83) Sprayed by the powder pistol.	74 71	7.7 8.1	— 221 — 188	<i>o</i> <i>o</i>	100 100	100 80
(1.93) Sprayed by the wire pistol.	52 61	5.6 6.9	— 1 — 5	<i>f</i> <i>f</i>	0.2 0.1	1 0.1	<i>B</i> <i>B</i>	... <i>w</i>	{ Up to 0.5% fine pits in the coatings.
(2) <i>Cadmium Coatings.</i>											
(2.23) Electrodeposited, cyanide bath.	229 202	5.0 5.0	— 20 — 18	<i>f</i> <i>f</i>	2 2	1 1	<i>B</i> <i>B</i>	<i>W</i> <i>W</i>	...
(2.73) Sprayed by the molten-metal pistol.	135 124	3.9 3.8	6 12	<i>f</i> <i>f</i>	2 0.05	1 0.5	<i>B</i> <i>B</i>	<i>W</i> <i>W</i>	...
(3) <i>Cadmium-Zinc (82/18) Alloy Coating.</i>											
(3.73) Sprayed by the molten-metal pistol.	105 76	3.3 2.3	— 122 — 102	<i>o</i> <i>o</i>	50 70	98 90	<i>B</i> <i>B</i>
(4) <i>Zinc Coatings.</i>											
(4.23) Electrodeposited, cyanide bath.	186 180	5.0 5.0	— 64 — 57	<i>x</i> <i>x</i>	{ Light grey colour, slight calcareous surface deposit.
(4.43) Hot-dipped (Firm A).	153 164	4.4 4.7	— 55 — 50	<i>x</i> <i>x</i>	{ Darker grey colour, slight calcareous surface deposit.
(4.53) Hot-dipped (Firm B).	192 193	5.6 6.0	— 48 — 53	<i>x</i> <i>x</i>	{ " " " "
(4.73) Sprayed by the molten-metal pistol.	159 82	5.7 2.5	— 26 — 34	<i>f</i> <i>f</i>	0.1 0.03	0.5 0.5	{ As for (4.23). Deposit tends to follow the spray lines.
(4.83) Sprayed by the powder pistol.	254 300	8.4 10.1	— 19 — 9	<i>f</i> <i>f</i>	0.2 0.02	{ Up to 2% fine blisters and pits in the coatings.
(4.93) Sprayed by the wire pistol.	113 120	3.9 3.9	— 39 — 41	<i>x</i> <i>x</i>	{ As for (4.73).
(5) <i>Lead Coatings.</i>											
(5.13) Electrodeposited.	313 311	4.2 4.2	— 79 — 56	<i>f</i> <i>f</i>	0.2 0.5	0.5 0.5	... 6C	6C 2.6C	<i>B</i> <i>B</i>	<i>w</i> <i>W</i>	{ The pits are few and near the suspension holes.
(5.73) Sprayed by the molten-metal pistol.	376 100	6.1 1.7	— 631 — 153	<i>o</i> <i>o</i>	98 50	98 40	... 0.6C	... 0.6C	... <i>B</i>	... <i>w</i>	
(6) <i>Lead-Tin (88/12) Alloy Coating.</i>											
(6.73) Sprayed by the molten-metal pistol.	79 80	1.7 1.7	— 257 — 172	<i>o</i> <i>o</i>	70 30	10 10	0.8C 0.6C	0.8C 0.6C	<i>b</i> <i>B</i>	<i>w</i> <i>w</i>	{ Rusting follows the spray lines.
(7) <i>Tin Coating.</i>											
(7.13) Electrodeposited.	211 208	4.8 4.7	— 36 119	<i>o</i> <i>f</i>	20 5	30 5	1.9F 2.1F	1.7F 2.1F	<i>B</i> <i>b</i>	<i>w</i> <i>W</i>	
(7.73) Sprayed by the molten-metal pistol.	94 94	2.7 2.8	— 234 — 135	<i>o</i> <i>o</i>	40 15	25 10	1.2C 1.2C	1.2C 0.6C	<i>b</i> <i>B</i>	<i>w</i> <i>w</i>	
(8) <i>No Coating. Pickled Steels.</i>											
(X2) Standard mild steel.	— 307 — 277	100 100	100 100	{ The mean loss in weight, 292 g., is equivalent to an average corrosion rate of 0.0035 in./year.
(K) Mild steel; Cr 1%.	— 281 — 283	100 100	100 100	{ Mean loss in weight, 282 g.
(N) Mild steel; Cr 0.9, Cu 0.5%.	— 309 — 283	100 100	100 100	{ Mean loss in weight, 296 g.

* T_m Coating thickness, mils. Average value obtained by the electromagnetic meter (see Appendix B).

† On exposure, i.e., the difference between the final weight after scraping off the marine growth and washing in fresh water, and the initial weight. In several cases a gain in weight was observed; this is indicated by a positive figure.

‡ In accordance with the scale used for the atmospheric specimens. These grades apply to both the front and back of each specimen.

§ A leader (...) indicates the complete absence of rust.

|| The maximum pit depth (mm.) is given together with an indication of the general size of the pits classified thus:

F Fine pits, up to 2 mm. dia.

M Medium pits, 2–10 mm. dia.

C Coarse pits, over 10 mm. dia.

A leader (...) indicates that the pitting, if any, was less than 0.2 mm. deep.

** Hard-bodied fouling organisms remaining after cleaning are indicated.

b Up to 50 barnacles per specimen, *B* more than 50.*w* Up to 50 tubeworms per specimen, *W* more than 50.

The fouling of the unprotected specimens was not recorded.

should be remembered that those responsible for their production make no such claim, as these coatings are primarily intended for heat-resisting purposes.

Sprayed Coatings.—Those applied by the wire pistol have so far given the best results. The thin coatings exposed at Sheffield have failed, but the medium and thick coatings are virtually intact at all the sites. At recent inspections slight blistering of the type illustrated in Fig. 2 has been observed on these coatings but this has as yet had no effect on their protective properties. A similar form of attack on aluminium coatings applied by the wire pistol has been reported by Britton and Evans.²

It is clear from Fig. 20 that the aluminium coatings sprayed by the molten-metal pistol have also behaved well in relation to the weight of coating. They seem prone to show early signs of breakdown but failure does not usually follow for a considerable period.

(c) Cadmium Coatings.

The relationship between life until failure (L_0) and coating weight (W) for the cadmium coatings exposed at Sheffield is shown in Fig. 21. All the eighteen specimens exposed have failed and it will be clear that the lives of the coatings depend chiefly on their weights, the method of application being of much less importance. Two of the electroplated specimens had been given a chromate rinse before exposure but this produced no appreciable effect.[†] The failure of cadmium coatings is illustrated by Fig. 10, which shows a specimen sprayed with cadmium by the molten-metal pistol after an exposure of 1.6 years at Sheffield.

(d) Cadmium-Zinc (82/18) Coatings.

Only eight cadmium-zinc alloy (82/18) coatings were exposed at Sheffield and all failed in less than 2 years. The behaviour of these coatings was

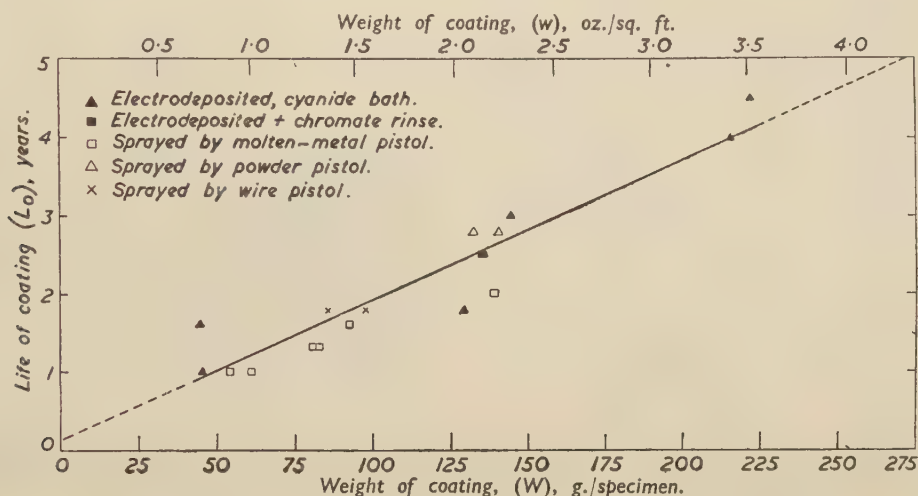


FIG. 21.—Lives of Cadmium Coatings Exposed at Sheffield.

It will be seen from Table II. that the medium and thick aluminium coatings sprayed by the powder pistol have given poor results at all stations. This may have been due partly to the use of an unsuitable grade of aluminium powder containing 3.3% of copper.* Failure occurred generally as a result of crumbling and disintegration of the coating metal, as is illustrated by Fig. 3, which shows a specimen after 1.6 years' exposure at Sheffield. The thin coatings applied by this method behaved better at Sheffield than the thick coatings; in fact, as is shown by Fig. 20, the thin coatings sprayed by the powder pistol had a life comparable with that of similar coatings sprayed by the molten-metal or wire pistols.

* See Table VII.

† See Appendix A. The rinse was a simple solution of chromic acid and the treatment used is not comparable with the proprietary chromate treatments applied commercially to zinc-coated articles or zinc-base die castings.

essentially similar to that of the cadmium coatings, the lives of the two types of coating, weight for weight, being substantially the same.

(e) Zinc Coatings.

Fig. 22 refers to the zinc-coated specimens exposed at Sheffield and shows the lives until failure (L_0) plotted against the weights of coating (W) and w . It is clear that, as in the case of cadmium, the lives of the coatings depend chiefly on their weight, so that differences in the method of application have, at the most, a secondary effect. All specimens with coating weights exceeding 110 g. (1.7 oz./sq. ft.) have a life exceeding 5.0 years.

One important difference in the behaviour of the coatings—attributable to the process of application—was, however, observed and may be illustrated by the Sheffield results (Table II.). It will be seen that the sherardized and the hot-galvanized coatings show signs of breakdown for a considerable period before the point of failure is reached, whereas in general the electrodeposited and the sprayed coatings fail within a comparatively short time of first showing signs of breakdown. The explanation is that the corrosion of the iron-zinc alloy present in the former coatings but not in the latter, results in a yellow-brown colour, which is reported as “discolouration or rust-staining of the coating,” and the grading of the specimens suffers accordingly. In the case of sherardized coatings, which consist almost wholly

No failure of a zinc coating has yet been observed at any of the exposure stations other than Sheffield, which is further evidence of the long life of zinc coatings in non-industrial atmospheres.

The main result to date of the present tests on zinc coatings is to show that the life until failure depends chiefly on the weight of zinc in the coating and that on this basis no significant effect due to the presence of iron-zinc alloy in certain types of coating has yet been detected. It will be noted that in Fig. 22 the points for the sherardized or cemented specimens and for some of the hot-galvanized ones lie slightly above the average straight line. At this stage it is difficult to decide how far these slight differences are significant. Further work on zinc coatings by the Protective Coatings Sub-Committee in collaboration with the

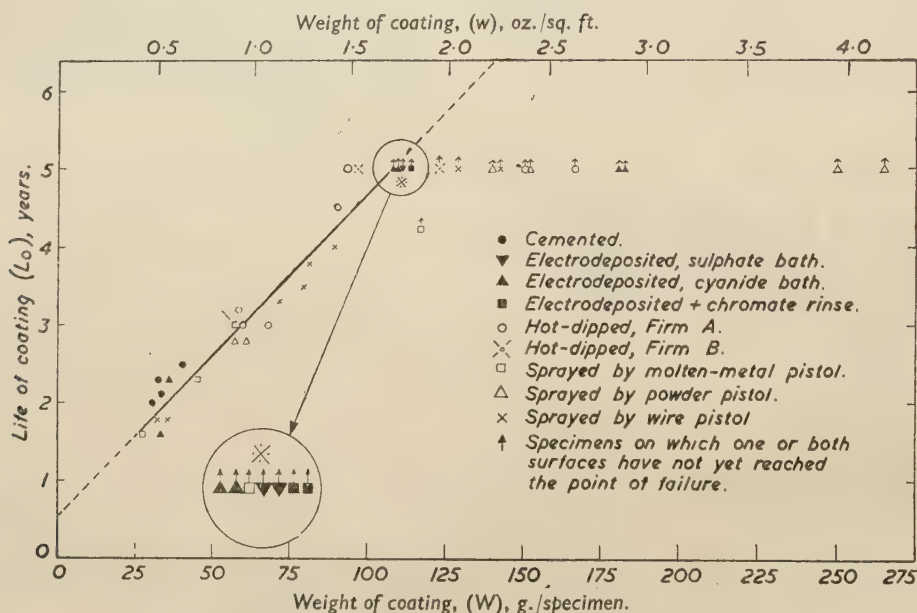


FIG. 22.—Lives of Zinc Coatings Exposed at Sheffield.

of iron-zinc alloy, this colour is noticed soon after exposure, whilst on hot-galvanized coatings, which consist of a similar alloy layer (or layers) and an outer zinc layer, the colour develops as soon as the zinc layer has corroded away and exposed the alloy layer. The discolouration resulting from the corrosion of the iron-zinc alloy layer is illustrated by the photograph of a hot-galvanized specimen that has just failed, reproduced in Fig. 4. This should be compared with Fig. 5, showing a zinc-sprayed coating at the point of failure, and Fig. 6 which shows an electrodeposited zinc coating intact.

It should be added that the application of a simple chromic acid rinse to certain of the electrodeposited zinc coatings had no marked effect on their performance, as was also the case for cadmium coatings (see section 5(c)).

British Non-Ferrous Metals Research Association is, however, in progress and may elucidate the matter.

In view of the importance of the subject, it may be of value to digress for a short period to consider the results of tests by other investigators that have a bearing on this point.

(i) *Tests by the American Society for Testing Materials on Hot-Galvanized Corrugated Sheets.*

In 1926, Sub-Committee VIII. of Committee A5 (Corrosion of Iron and Steel) of the American Society for Testing Materials commenced a series of atmospheric-exposure tests on hot-galvanized corrugated iron or steel sheets at various stations in the United States. The results of some of these tests are shown in Fig. 23, where the time required for the appearance of rust (corresponding

to about 1% of rust) is plotted against the coating weight. It will be seen that the relationship is linear at all three corrosion stations.*

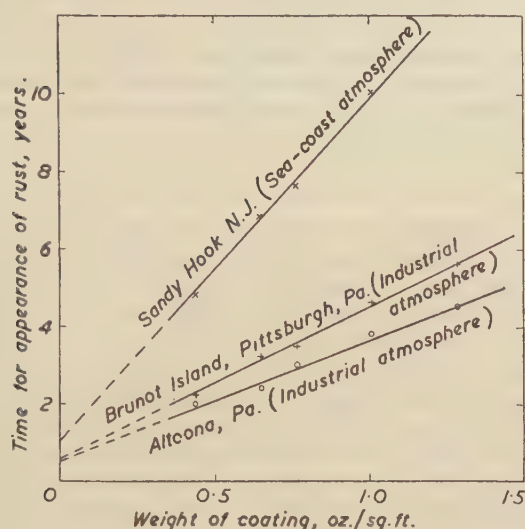


FIG. 23.—Results of Atmospheric-Exposure Tests on Hot-Galvanized Iron or Steel Sheets. (American Society for Testing Materials.)

At a later date (1936–1937) the same A.S.T.M. Sub-Committee undertook an elaborate series of atmospheric-exposure tests on fencing wires, the bulk of which were zinc-coated. A complete chemical and physical examination was made of all the original materials and coatings. An analysis of the interim results of these tests, which relate to the most corrosive station only (in this case the industrial atmosphere of Brunot Island, Pittsburgh) shows that under these conditions the lives of zinc coatings on wires of approximately $\frac{1}{8}$ in. dia. can be adequately represented by the relationship:

$$l = 2.6w + 0.6$$

Here l is the life of the coating in years—in this case taken as the mean of the exposure periods required for the development of 1% of rust and of 100% rust, respectively, and w is the weight of the zinc coating in oz./sq. ft. The calculation is based on data published by Committee A5 (A.S.T.M.).³

The great majority of the zinc coatings on these wires were applied by hot-galvanizing and the percentage of iron in the coating itself varied from approximately 1 to 9%, according to the coating thickness and the source of supply. There are a few wires, however, of which the iron content of the coatings is about 0.1% or less, and which were presumably coated by electrodeposition. Detailed examination of the results does not reveal any marked discrepancy between the behaviour

of these wires and that of the remainder of the specimens tested, but it is clear that a final conclusion as to the relative merits of the two types of coating could be based only on tests in which electrodeposited coatings were more evenly represented.

(ii) *Tests by C. E. Richards (Post Office Research Station.)*

In 1938, Richards published the results of an extensive investigation of the atmospheric corrosion of galvanized iron wire.⁴ This included a wide series of field tests on wires carrying different coating weights of zinc and which were exposed at numerous stations in this country. Richards also observed a linear relationship between life and coating weight and remarks: "The predominating factor in the life of a galvanized wire in a given atmosphere is the thickness of the zinc envelope and characteristics such as the purity and ductility of this coating are of minor importance."

The field tests were concerned with two series of nine lots of wire, of 8 and 14 S.W.G., respectively. Of these, one lot of each gauge was electrodeposited and the remainder were hot-galvanized. It is an interesting fact that when converted to the basis of equal coating weight, the results for these electrodeposited wires (No. 16) were certainly no worse than those for the other specimens. This is shown by the data given in Table V., which have

TABLE V.—Effective Lives of Zinc Coatings, Years per Ounce per Square Foot (C. E. Richards).

Average values for 8 exposure stations in England.

Wire Lot No.	8 S.W.G.		14 S.W.G.	
	Fe in Coating, %.	Effective Life, years/oz./sq. ft.	Fe in Coating, %.	Effective Life, years/oz./sq. ft.
11	3.6	3.1	2.5	3.0
12	3.9	2.9	2.9	2.7
13	2.5	2.5
14(a)	5.8	3.0
15	4.9	2.6
15(a)	4.0	2.6
15(b)	2.8	2.5
16	0.3	3.3	0.3	2.9

been calculated from the figures given in the original paper.

(iii) *Summary of Observations on the Atmospheric Corrosion of Zinc Coatings.*

The following statement would seem to be a fair summary of the observations made in the course of the present work and of those of the other investigators referred to above:

* See also Report of Sub-Committee VIII. of Committee A5 on Field Tests of Metallic Coatings, C. E. Reinhard, *Proceedings of the American Society for Testing Materials*, 1944, vol. 44, p. 92.

(1) The life in an industrial atmosphere of a zinc coating on iron or steel is essentially proportional to its weight.

(2) The effects of different methods of application of the zinc coating are of a secondary order as compared with that of coating weight.

This statement assumes, of course, that the coatings are correctly applied and that both they and the conditions of atmospheric exposure are reasonably uniform. It is strictly applicable only to the range of coatings tested (*i.e.*, the possibility of finding zinc coatings with improved corrosion resistance is not precluded) and to the range of coating weight so far tested to failure, *viz.*, 0.4–1.7 oz. of zinc per sq. ft. of surface. It may be that coatings below this range would fail more rapidly and that those above it may have a longer life than would be indicated by a purely linear relationship, but fuller experimental results are needed to decide these points.

(f) *Lead Coatings.*

At Sheffield none of the lead coatings has yet reached the point of failure, though many became discoloured or rust-stained a short while after exposure and are now graded as "fair." Some of the rust-staining is extensive, particularly on the specimens with thin coatings (Fig. 7); this is presumably caused by pores in the coatings permitting attack on the basis steel, while the lead, being cathodic to iron, remains virtually un-attacked. In this way a lead coating becomes rusted through instead of corroding away from the outside as, for instance, does a zinc coating. Owing to this mode of breakdown, it is difficult to decide when a surface has reached the point of failure, particularly at Sheffield where all the specimens become covered with grime. For a time many of the lead-coated specimens at Sheffield showed a nearly white surface deposit; it seems reasonable to assume that this consisted essentially of lead sulphate, and resulted from the corrosive attack of the sulphur gases present in this highly polluted industrial atmosphere. After 5 years' exposure the specimens are now nearly black, a layer of soot and dirt covering the white deposit.

Elsewhere the lead-coated specimens are discoloured generally or rusted at small spots. The thin coatings exposed at Llanwrtyd Wells and Calshot failed after the relatively short periods of exposure of 1.0–1.6 years, and these specimens have not behaved as well as the corresponding ones at Sheffield as will be seen by comparing Figs. 7, 8, and 9. In all probability this is because in the case of the specimens at Llanwrtyd Wells and Calshot there is no formation of a sulphate film which evidently increases the protective value of lead coatings in industrial atmospheres.

Only a few of the medium and thick lead coatings exposed elsewhere than at Sheffield have reached the point of failure; the rusting on the others is spreading slowly and it may be that failure will be deferred for some time. Some of these coatings have developed blisters (Fig. 9) but in general the mode of failure is the same as at Sheffield, *i.e.*, the rusting-through of the coating spreading from small spots.

(g) *Lead-Tin (88/12) Coatings ("Terne").*

The behaviour of the lead-tin (88/12) coatings has not differed appreciably from that of the lead coatings and the remarks made in the previous section are generally applicable to the lead-tin coatings as well. The latter have failed less rapidly at Sheffield than at Llanwrtyd Wells where they show discolouration and rust-staining. Only one specimen of this type has yet reached the point of failure at Sheffield and the number of specimens exposed elsewhere is too small to permit of a quantitative comparison of the alloy coatings with those of lead or tin.

(h) *Tin Coatings.*

The results obtained with tin coatings are similar to those described above for lead and lead-tin coatings inasmuch as the method of failure by rusting through the coating was the same (Fig. 11) and failure has occurred more rapidly at Llanwrtyd Wells and Calshot than at Sheffield. On the whole the results of the tests in an industrial atmosphere are less satisfactory for tin than for lead or lead-tin (88/12) alloy as six of the eight specimens sprayed with tin have failed on both surfaces and the other two on one surface, whereas only one of the specimens coated with lead-tin alloy and none of those coated with lead has failed after 5 years' exposure at Sheffield. The sprayed tin coatings showed extensive rust-staining after short periods of exposure, as is illustrated in Fig. 12. It seems, therefore, that tin coatings are relatively more sensitive to differences in the method of application. Presumably the superiority of the hot-dipped and electrodeposited tin coatings to the sprayed tin coatings at Sheffield, is due to the more porous nature of the sprayed coatings.

(i) *General Comparison of the Different Metals and Alloy Coatings.*

Metals and alloys applied as protective coatings to steel may be classified in two groups, according to whether their electrochemical relationship to steel is such that they tend or do not tend to prevent corrosion of the steel base at breaks in the coating. Coatings of the former group, *i.e.*, those which exert electrochemical protection, are known as anodic coatings, those of the latter, which do not, as cathodic coatings. In general,

failure of the protective properties of anodic coatings is delayed until the coating metal itself has corroded away and exposed the steel over areas of appreciable size, whereas cathodic coatings usually fail by permitting or indeed by intensifying the development of rust at breaks in the coating; this type of attack associated with cathodic coatings is particularly dangerous, as it may give rise to serious pitting.*

On the basis of their behaviour in the present tests, coatings of aluminium, cadmium, cadmium-zinc (82/18), and zinc are classed as anodic, and coatings of lead, lead-tin (88/12), and tin as cathodic. It will be noted that cadmium has been included with zinc and aluminium as being anodic to iron, whereas according to the electrochemical series of the metals† it is slightly cathodic. As pointed out by Evans,⁵ however, the polarity depends on conditions and does not always follow the electrochemical series. The case of cadmium coatings on steel has been considered from the theoretical angle by Hoar,⁶ who shows that polarization causes the cadmium to behave anodically.

The results obtained with the various metals differ according to the type of atmosphere, and will therefore be considered separately.

(i) *Non-Industrial Atmospheres.*

At the atmospheric-exposure stations other than Sheffield most of the anodic coatings are giving good results; in the case of aluminium this applies only to the coatings sprayed by the wire or molten-metal pistols. The cathodic coatings are generally showing a much greater tendency to fail. There is no doubt that up to the present the anodic coatings have proved superior to the cathodic ones in these non-industrial atmospheres. It is not possible to assess the relative merits of the four anodic coating metals, as there is little breakdown so far. Of the cathodic coatings, lead and lead-tin (88/12) are on the whole giving better results than tin.

(ii) *Industrial Atmosphere.*

In connection with the specimens exposed in the highly polluted industrial atmosphere at the Sheffield corrosion station the position is not so clear. The best coatings to date on the basis of their lives until failure (5% rusted) in relation to their thicknesses are those of lead and lead-tin (88/12), the tin coatings giving similar but slightly inferior results. Many of these coatings are discoloured or rust-stained (Figs. 7 and 12) while the lead coatings are covered with a film—apparently of sulphate—and it is impossible to

predict with any certainty when final failure will occur. It will be noted that all these coatings are cathodic to steel.

The anodic coatings on the other hand have so far given results in accordance with their coating thicknesses, with the reservation that for aluminium this holds good only for the coatings sprayed by the wire or molten-metal pistols. All the cadmium coatings have failed. The thin aluminium and zinc coatings have also failed, but the thicker coatings of these metals do not yet show appreciable signs of breakdown.

It is advisable to defer comparison between the anodic and the cathodic coatings at Sheffield until more specimens have failed. All that can be said at present is that the thin cathodic coatings have given longer lives than the thin anodic coatings, but that the appearance of the thicker anodic coatings (aluminium and zinc) is better than that of the thicker cathodic coatings (lead and lead-tin).

A fairly reliable comparison between the various anodic coatings at Sheffield can be made by calculating (by the method of least squares) the equations of the most probable straight line fitting the experimental results. These lines have been drawn for aluminium, cadmium, and zinc coatings and are reproduced in Figs. 20, 21, and 22. All points referring to specimens that have not yet failed were ignored and in the case of aluminium, only the points relating to the coatings sprayed by the wire pistol, the molten-metal pistol, and the thin coatings sprayed by the powder pistol have been used in the calculation.

The equations are as follows :

$$\begin{aligned}\text{Aluminium: } L_o &= 0.08W + 0.9. \\ \text{Cadmium: } L_o &= 0.018W + 0.1. \\ \text{Zinc: } L_o &= 0.041W + 0.5.\end{aligned}$$

where L_o = life of coating to grade "failed," years.

Mean value for the front and back surfaces, and

W = weight of coating, g./specimen.

The general usefulness of these equations will be increased by expressing them in two other forms, as below :

$$\begin{aligned}\text{Aluminium: } L_o &= 5.1w + 0.9. \\ \text{Cadmium: } L_o &= 1.1w + 0.1. \\ \text{Zinc: } L_o &= 2.6w + 0.5.\end{aligned}$$

$$\begin{aligned}\text{Aluminium: } w &= 0.20L_o - 0.2. \\ \text{Cadmium: } w &= 0.92L_o - 0.1. \\ \text{Zinc: } w &= 0.39L_o - 0.2.\end{aligned}$$

where L_o = life of coating, years, as above, and
 w = weight of coating, oz./sq. ft. of surface.

* Cf. the results given in section (6) for lead, lead-tin (88/12) alloy, and tin coatings completely immersed in sea-water.

† The normal electrode potentials of the metals concerned are : Al, -1.67 ; Zn, -0.76 ; Fe, -0.44 ; Cd, -0.40 ; Sn, -0.14 ; Pb, -0.13 V.

It will be noted from Figs. 20, 21, and 22 that the lines when extended indicate that a coating of zero weight would have an appreciable life, which is, of course, incorrect. The same discrepancy occurs in the results of other investigations (*cf.* the American results shown in Fig. 23), and its probable causes are :

(1) The lives of thinner coatings are not necessarily comparable with those of the coatings tested.

(2) There is a lag in reporting failure, as the specimens are inspected only at 6-monthly intervals; thus a surface that reached the point of failure after 1.6 years' exposure would be graded as fair when inspected after 1.5 years and as failed only when inspected after 2.0 years—its life thus being reported as 2.0 years.

By inserting in these equations the value of 5 for L_0 , we obtain values for W or w which represent the weight of coating necessary to ensure a life to failure (5% of surface rusted) of 5 years. The results are given in Table VI. In

TABLE VI.—Coating Weight and Thickness Required for a Life of 5 Years at Sheffield to 5% Surface Rusted.

Metal.	Density, g./c.c.	Coating Required.		
		Weight,		Equivalent Thickness, mils.
		W , g./specimen.	w , oz./sq. ft.	
Aluminium .	2.70	51	0.8	3.6
Cadmium .	8.64	272	4.5	6.0
Zinc .	7.16	110	1.7	2.9

this Table the equivalent thickness of the coating metal has been calculated from its weight on the assumption that the metal has the normal density; this is not always the case because with some methods of application the coatings are porous, and with others diffusion into the steel base occurs.

It should also be noted that the figures given for coating weight are to be regarded as average values rather than as minimum values at any given point. This is because most of the coatings were prepared under normal industrial conditions with the result that there were considerable local variations in coating thickness over any one surface and, in some cases, even more appreciable differences between the fronts and backs of the specimens; these differences were revealed by the initial coating-thickness measurements made with an electromagnetic thickness meter (*see* Appendix B). It is considered that, as regards the practical interpretation of the experimental results, this variation should, within reason, take care of such

variations in coating thickness as may occur on a commercial article protected by a metallic coating, with the possible exception of small parts and articles of unusually complicated shape.

The following observations may be made regarding the data summarized in Table VI. which, it will be recalled, relate to an industrial atmosphere :

(1) Cadmium is less satisfactory than aluminium or zinc, whether the comparison is made on the basis of weight or of thickness of coating. Aluminium and zinc are equal as regards the necessary thickness of coating, but aluminium is superior when the weight of coating is considered. It should be borne in mind that of the aluminium coatings tested only those sprayed by the wire pistol or the molten-metal pistol have given a life as long as 5 years at Sheffield; of these two pistols the wire pistol is preferred because the coatings applied by the molten-metal pistol showed earlier signs of rust-staining.

(2) The superiority of zinc coatings on iron compared with cadmium coatings in industrial atmospheres is in agreement with the results of other investigators. For instance, Passano⁷ states that in atmospheric-exposure tests in New York City, cadmium coatings were found to weather 2.6 times more rapidly than zinc coatings; in other atmospheric tests on electro-deposited coatings then in progress at the Bureau of Standards, a cadmium coating of 0.36 oz./sq. ft. of surface had given about the same service as a zinc coating of 0.12 oz./sq. ft. of surface.

The contrary view, which was current some years ago, was based on the results of laboratory spray tests. The colour and appearance of cadmium coatings is in their favour, however, and it is possible that under other conditions of exposure, the use of cadmium coatings might be justified, particularly where relatively thin coatings were concerned.

(3) The good behaviour of aluminium coatings is in agreement with the low rate of corrosion of this metal found in atmospheric tests⁸ and confirms the earlier results reported by Britton and Evans for aluminium coatings sprayed by the wire pistol.⁹

(4) The figure deduced for the coating weight of zinc required to give 5 years' protection against corrosion at Sheffield (1.7 oz./sq. ft.) is in reasonably good agreement with the results obtained by other observers. For instance, Passano⁷ (*loc. cit.*, p. 31) states that the weight of zinc coating needed to give protection for 5 years to the 5% rust stage is 1.25 oz./sq. ft. at Altoona or 1.0 oz./sq. ft. at Pittsburgh, both industrial atmospheres. Richards⁴ (*loc. cit.*, p. 153 p, Table XV.) found the effective lives of

coatings per ounce per square foot as applied to wires of 8 S.W.G. to be 1.95 years at Widnes and the average value for six other industrial atmospheres to be 3.11 years; by simple proportion the approximate coating weight for a life of 5 years would be 2.6 oz./sq. ft. at Widnes and 1.6 oz./sq. ft. at the other industrial stations. From the results of exposure tests of 1 year on small specimens of solid zinc, one of the authors deduced that a zinc coating of 2 oz./sq. ft. should have a life of 5 years at Sheffield.¹⁰

If the inevitable differences in corrosive conditions from one exposure station to another are taken into consideration, all these observations are sufficiently concordant to suggest that when the nature of the article permits of it, zinc coatings applied to iron and steel for use outdoors in industrial atmospheres should be of the order of 2 oz./sq. ft. of surface.

In non-industrial atmospheres the lives of zinc coatings are much greater than at Sheffield, which is in agreement with the known lower corrosion rate of zinc at such sites.¹⁰ In this connection, Schikorr¹¹ has shown that in Berlin the rate of corrosion of zinc coatings on wires is much greater in winter than in summer and increases with the sulphur content of the atmosphere.

In conclusion it may be remarked that, of the coating metals tested, zinc is that most generally useful for the protection of iron and steel against atmospheric attack. Since zinc is anodic to iron, it has the advantage of providing a reasonable amount of protection at discontinuities or imperfections in the coating, so that pitting attack on the basis metal is rendered improbable. Another point in its favour is that all the methods of application tested have so far given good results in relation to the weight of zinc applied, which has been shown to be the chief fact in determining the life of the coating at Sheffield. It is interesting to note, as illustrating the cathodic protection afforded by zinc, that Richards⁴ (*loc. cit.*, p. 146 P) obtained a similar result for galvanized wires on which the coating had been cracked by bending the wires before exposure; the coatings exposed in the present tests were undamaged.

(j) *General Comparison of the Different Methods of Application.*

It may be helpful to add a few comments, not covered by the previous remarks, with regard to the different methods of applying the metallic coatings.

(i) *Cemented Coatings.*

Cementation proved a suitable method of applying thin zinc coatings, which had lives in proportion to their weight, but cemented aluminium

* See Tables X. and XI.

coatings gave poor results under these particular exposure conditions.

(ii) *Electrodeposited Coatings.*

As a method of application, electrodeposition has the advantage of permitting close control of the coating thickness, particularly on articles of simple shape. This was so in the present tests.*

The surface of the $15 \times 10 \times \frac{3}{8}$ -in. specimens used in these experiments was rougher than is usual for electroplating and the behaviour of the lead coatings at Llanwrttyd Wells and Calshot, but not so far at Sheffield, has been adversely affected by this factor, as rusting was observed to commence at and spread from the rolling scratches present in the steel base, which were subsequently opened up by the pickling process preparatory to electroplating. The surface roughness may have affected the porosity of the coatings; if so, their protective properties—particularly in the case of the cathodic metals (lead and tin)—may not prove as good as those attainable on smoother surfaces. There is, however, no evidence that the performance of the cadmium- or zinc-plated coatings has been affected in this way and it should be remembered that the specimens tested are typical of hot-rolled heavy structural steel, the object of this investigation.

No difference has been observed between zinc coatings deposited from the sulphate or from the cyanide bath, when compared on the basis of equal coating weight.

(iii) *Hot-Dipped Coatings.*

Hot-dipping as a process has given best results with zinc. Hot-dipped aluminium coatings have not behaved well under these conditions of exposure, while the hot-dipped lead, lead-tin (88/12) alloy and tin coatings were all thin, which has no doubt militated against their satisfactory performance.

(iv) *Sprayed Coatings.*

Metal spraying has shown itself a valuable method of applying coatings of any of the metals and alloys tested. The only difference yet revealed between the three types of pistol, as far as corrosion resistance is concerned, is that the powder pistol cannot be recommended for aluminium coatings.† With this exception, the sprayed coatings of the metals anodic to steel have given results at all stations comparable, on the basis of equal weight, with those given by other methods of application. Sprayed metal coatings are of a porous character; in the case of the cathodic coating metals this had led to more rust-staining than on the less porous hot-dipped or electroplated coatings. The lives until failure

† But see the Discussion and also p. 241 P.

of the sprayed coatings have not, however, been markedly affected by this staining in relation to coatings of the same weights applied by other methods.

Rusting of sprayed coatings often commenced on areas which formed a more or less regular pattern on the surface, as shown by Figs. 5, 10, and 12. Clearly, these areas are where the coating was thinner than the average, being left between successive strokes of the pistol when the specimen was sprayed; this feature of metal-spraying depends largely on the operator. Incidentally, under some circumstances this control by the operator may be an asset, as it enables thicker coatings to be applied at places where corrosion is likely to be intensified.

(v) *Conclusions.*

The vague but satisfactory general conclusion emerging from this discussion is that all the various methods of applying metallic coatings have their uses. For any particular purpose the choice between them will be governed partly by the desired protective properties of the coating itself, but also to a large extent by such factors as the coating metal to be used, the conditions of service, the size and shape of the article to be coated, and, last but by no means least, considerations of cost.

(k) *Composite Protective Schemes (Metallic Coatings plus Paint).*

The preceding remarks made in this section have referred to metallic coatings exposed as they stood, *i.e.*, without further protection by means of paint. In conclusion a few comments will be added regarding the behaviour of specimens on which the metallic coating was supplemented by two coats of red oxide paint. Details of the specimens concerned will be found in Table III., while the formulation of the red oxide paint is given in Appendix A.

Unfortunately, the red oxide paint concerned had been in stock for some time and in and after use it became evident that its application and drying properties had deteriorated. In fact it is now clear that careful consideration is necessary in the choice of painting schemes for application over metallic coatings and it is improbable that a simple red oxide in linseed-oil paint is the most suitable for the purpose. With this reservation, it may be noted that none of the protective schemes in this group has yet failed as a whole. At Sheffield, after 5 years' exposure, there is marked cracking and peeling of the paint where this has been applied over zinc coatings. This breakdown of the paint film is most marked on the hot-dipped specimens, despite the fact that they had been treated before painting with a surface wash consisting of a mixture of hydro-

chloric acid and organic solvents; on these specimens the paint has now ceased to afford any appreciable protection and the zinc coating alone remains effective. The maximum life of the paint film itself over a zinc coating was observed where the zinc coating had been applied by spraying.

It is an interesting fact that the paint is still in good condition generally on the aluminium and lead coatings, and has remained intact and effective. In the case of the lead coatings, one specimen of each pair was treated with a phosphoric acid wash before painting. This consisted of a 35% solution of phosphoric acid (sp. gr. 1.70) in methylated spirit (61 O.P.). It was applied by brush, allowed to dry for $\frac{1}{2}$ hr., and washed-off with hot water, the first coat of paint being brushed on when the specimens had dried again. This treatment had no effect on the results and seems to be unnecessary.

6.—DISCUSSION OF THE RESULTS OF THE TOTAL-IMMERSION TESTS IN SEA-WATER.

(a) *Fouling.*

When the specimens were removed from Gosport after 2 years' immersion in sea-water, those coated with zinc were covered with mud and slime and the remainder with a thick layer of mud, slime sea-squirts, and sponges, in which barnacles and tubeworms were hidden. Marine plants were absent, presumably because the specimens had been shielded from daylight by the landing stage under which they were exposed.

A rough count of the number of barnacles and tubeworms that remained attached to the specimens after cleaning is given in Table IV. This illustrates the interesting fact—readily apparent from visual inspection at the time—that the degree of fouling is influenced by the nature of the metallic coating. With two exceptions, all the zinc-coated specimens were entirely free of both barnacles and tubeworms, whilst, in the main, shell fouling on the specimens sprayed with cadmium-zinc (82/18) alloy was confined to a heavy growth of barnacles. The cadmium, lead, lead-tin (88/12), and tin coatings were markedly fouled by both types of organism.

It may be concluded that zinc has a toxic or deterrent effect in relation to fouling by shell organisms, although it cannot be ranked in this respect with the anti-fouling agents proper, such as the compounds of copper and mercury.

(b) *Protection.*

The relative merits of the protective schemes tested are shown in Table IV. by the gradings of the surfaces, together with the figures for rusting and pitting; the changes in weight are of limited significance. It should be recalled, in considering

the following discussion, that in the case of metallic coatings a thick coating (5 mils) was aimed at throughout, although Table IV. will show that this figure was not always achieved.

(i) *Zinc.*

It is clear that the zinc coatings have given better results than any of the other metallic coatings; apart from slight rusting on some of the sprayed specimens, there is as yet little to choose between the various methods of applying the zinc. As already mentioned, these zinc-coated specimens have been re-immersed in sea-water at Emsworth, and it is hoped that differences, if any, between the methods of application will be revealed when further breakdown occurs.

(ii) *Aluminium.*

The aluminium coatings applied by spraying with the molten-metal pistol or the wire pistol were almost intact at the conclusion of 2 years' immersion, but the hot-dipped aluminium coatings and those sprayed by the powder pistol had failed; these results are in conformity with those of the atmospheric-exposure tests.

(iii) *Cadmium.*

The cadmium coatings behaved fairly well but had rusted more than the zinc specimens; those of cadmium-zinc (82/18) alloy had failed before the conclusion of the test.

(iv) *Lead.*

The lead coatings did not give satisfactory results. The specimens coated with lead by the molten-metal pistol rusted badly after 2 years and, although those on which the lead had been applied by electrodeposition were much better in this respect, they had suffered heavy pitting. This pitting was particularly marked near the suspension holes, probably because shielding here by the hooks which suspended the specimens in the electroplating bath had led to local and abnormal thinness of the lead coating, but pitting had also occurred along the line of the original longitudinal rolling scratches, which had been opened up by the pickling treatment prior to electrodeposition; this latter feature is illustrated in Fig. 13, in which barnacle seatings and tube-worms will also be noted. Thin or damaged areas can hardly be entirely prevented in coatings of a relatively soft metal such as lead and, as the tests show, under such circumstances there is a serious risk of heavy pitting of the basis steel if lead-coated parts are immersed in sea-water. One of the pits shown in Fig. 13 is nearly $\frac{1}{4}$ in. deep.

(v) *Lead-Tin (88/12) Alloy.*

This last comment also holds good for coatings of tin and lead-tin (88/12) alloy. The specimens with either of these coatings were more rusted than those coated with lead and were also pitted to a marked extent.

(c) *Corrosion of Unprotected Mild Steels.*

For control purposes, duplicate specimens of each of three mild steels were exposed without any protective coating, after the mill-scale had been removed by pickling in hot dilute sulphuric acid containing an inhibitor. One of these steels was the Corrosion Committee's standard mild steel X, containing 0.2% of carbon; the other steels, K and N, were similar in composition to this, except that K contained 1% of chromium and N 1% of chromium and 0.5% of copper. The losses in weight of these three steels on exposure* show no definite variation outside the range of experimental error and it may be concluded, in conformity with previous observations, that under these conditions of exposure—total and static immersion in sea-water accompanied by heavy fouling—the addition of small amounts of copper and/or chromium to mild steel has no marked effect on its resistance to corrosion. This is in contradistinction to the effects of such additions in the case of mild steel exposed to atmospheric corrosion outdoors, where the low-alloy steels are much more resistant to attack.¹²

7.—SUMMARY.

An account is given of the field tests of the Protective Coatings Sub-Committee on protective metallic coatings for ordinary irons and steels. These tests were made on specimens of mild-steel flats, each $15 \times 10 \times \frac{3}{8}$ in., and were conducted both in the open atmosphere and completely immersed in sea-water. The following interim conclusions are drawn from the results of observations over periods of up to 5 years in the case of the atmospheric tests or of 2 years in that of the sea-water tests.

(1) Zinc is the most generally useful metal for the protection of steel, both when freely exposed to the atmosphere or continuously immersed in sea-water. It possesses the advantages of being applicable by a number of different processes and of relatively high resistance to abrasion, coupled with the fact that it tends to protect the steel by sacrificial action if the coating is initially imperfect or is subsequently perforated by damage.

(2) The most important factor in determining the lives of zinc coatings in industrial atmospheres is the weight of zinc applied, the method of application being less important. Zinc coatings of

* The specimens were de-rusted before the final weighing. The rust was easily removed by hand-cleaning and wire-brushing; no chemical de-rusting treatment was necessary.

2.9 mils in thickness (1.7 oz. per sq. ft. of surface) had reached the point of failure (5% surface rusted) after 5 years' exposure at Sheffield; in rural or marine atmospheres the lives of zinc coatings have proved to be much longer, weight for weight.

(3) Zinc coatings of 5 mils in thickness (3.0 oz./sq. ft.) were still practically intact after 2 years' immersion in sea-water.

(4) Cadmium coatings are inferior to zinc coatings of the same thickness when exposed in an industrial atmosphere or when immersed in sea-water; no comparison is yet possible in the case of non-industrial atmospheres where the coating lives are much longer. The same rough proportionality between coating life and coating weight in an industrial atmosphere has been observed for cadmium as for zinc, but the thickness of coating required to give a life of 5 years (5% surface rusted) was 6.0 mils (4.5 oz./sq. ft.) for cadmium, as compared with 2.9 mils (1.7 oz./sq. ft.) for zinc.

(5) Aluminium coatings sprayed by the wire pistol or the molten-metal pistol protect steel well in the atmosphere or in sea-water; other methods of applying aluminium coatings for these purposes are not recommended. It is estimated that coatings 3.6 mils thick (0.8 oz./sq. ft.) sprayed by the wire pistol or the molten-metal pistol would reach the point of failure (5% surface rusted) after 5 years' exposure at Sheffield. In rural or marine atmospheres the lives of aluminium coatings applied by the recommended methods are longer.

(6) In the industrial atmosphere of Sheffield, coatings of lead and lead-tin (88/12) alloy ("terne") developed a surface film, presumably of lead sulphate. Only one of the coatings tested at this station, varying in thickness from 0.5 to 5 mils (about 0.5 to 5 oz./sq. ft.), had failed after 5 years' exposure. In non-industrial atmospheres poor results were obtained from thin coatings of both types; thicker coatings showed discolouration and rust spots at the most recent inspections (after 5 years), although failure is spreading only slowly.

(7) Lead, "terne," or tin coatings cannot be recommended for steel immersed in sea-water as severe pitting occurs when the coating becomes penetrated at thin or damaged places.

(8) Tin coatings give shorter lives than lead or "terne" coatings on steel exposed to the atmosphere or immersed in sea-water.

(9) Combinations of metallic coatings with paint (2 coats of red oxide paint) have behaved well under atmospheric conditions, especially when the metallic coating was sprayed aluminium or electrodeposited lead. The performance of the paint was not particularly good when applied over zinc coatings and it showed poor adhesion to hot-galvanized surfaces, despite the fact that an etching treatment was used. It is clear that care

is necessary in the choice of paints for application over zinc and other metallic coatings.

APPENDIX A.—*Preparation of the Specimens.*

(a) *Mild-Steel Flats.*

The 10 × $\frac{3}{8}$ -in. mild-steel flats used as a basis for the coatings under test were rolled from a 50-ton heat of ordinary mild steel produced in a basic open-hearth furnace. Full details of the process of manufacture were recorded at the time, but as these present no unusual feature, it is unnecessary to give them here. The analysis of the material was approximately 0.22% of carbon, 0.57% of manganese, 0.05% of silicon, with contents of phosphorous, sulphur, chromium, copper, and nickel each less than 0.05%.

The specimens were prepared from the flats by cold-sawing into 15-in. lengths; in order to avoid contamination of the surface no lubricant was used. The necessary steps were taken to ensure that the specimens reached the laboratory in a clean unruined condition with the mill scale intact.

As is usual in the Corrosion Committee's work, a number of specimens were subjected to chemical analysis, mechanical tests, and metallographic examination in a standard manner. The results showed that the material was entirely normal for this class of steel and revealed the presence of a rim about $\frac{1}{32}$ in. thick.

(b) *Application of the Coatings.*

Most of the coatings were applied to the specimens in the presence of one of the authors at works where the different processes were in commercial use. Whenever a preliminary treatment, such as pickling or shot-blasting was given, the specimens were weighed on the spot after this treatment and before the application of the coating proper, using a balance and weights belonging to the Committee; this procedure enabled the weight of the coating to be determined.

Details of the methods of applying the coatings were recorded through the courtesy of the firms concerned and the accounts of the various processes given below are made with their approval. They are classified on the basis of the method of application, e.g., cementation, electrodeposition, &c.

(c) *Cemented Coatings.*

Coatings of aluminium and zinc were applied by proprietary processes of the cementation or hot-diffusion type.

(i) *Aluminium, Cemented (1.0).*

This process is usually known as calorizing; it yields iron-aluminium alloy coatings that reduce the oxidation and scaling of steel at moderately high temperatures. It is not claimed that the

coatings are especially resistant to straightforward atmospheric corrosion outdoors.

The specimens were first descaled by shot-blasting in the usual way, using steel grit. After weighing, the specimens were packed with the calORIZING mixture into a retort which was rotated and heated for some hours. Details of the composition of the mixture and of the temperature and time of heating were not divulged. According to published information, however, the mixture consists of aluminium powder, aluminium oxide powder and small amounts of ammonium chloride, and the retort is heated to 700–900° C.

The coating was of a grey colour, without metallic lustre, and rough, having many granules about the size of a pin head on its surface.

(ii) *Zinc, Cemented (4.0).*

This process is usually known as sherardizing; it produces a layer of iron-zinc alloy on the surface of the steel with a thin outer layer of zinc. The normal thickness is about 0.7 mil, but the thickness can be controlled accurately from about 0.3 to 1.5 mils when required. The coating by itself is suitable for use under conditions that are not severely corrosive, and it also forms a good basis for subsequent coats of paint.

The specimens were first descaled by pickling in cold hydrochloric acid * followed by consecutive rinses in cold water, hot soda-ash solution, and again cold water, with a final rinse in hot water to ensure rapid drying without tarnishing. After weighing, the specimens were placed in steel containers together with zinc dust and sand (Fig. 14); the quantities of zinc dust and sand are varied according to the size of the container and the articles to be treated. The drum was closed, and heated in a furnace at 370° C. for 6 hr., being rotated whilst in the furnace at 6 r.p.m. The composition of the zinc dust is given in Table VII.

After coating, the specimens had a smooth mat, dark-grey surface.

(d) *Electrodeposited Coatings.*

The preparation of the electrodeposited coatings of cadmium, zinc, lead, and tin was undertaken at the Armament Research Department, Woolwich, by arrangement with Mr. A. W. Hothersall, and that of tin at the Tin Research Institute, by arrangement with Dr. E. S. Hedges and Mr. S. W. Baier. The conditions of electrodeposition are adequately defined by the particulars given in Tables VIII. and IX. in conjunction with the following notes:

(i) The surface of the hot-rolled flats, after descaling by pickling, was considerably rougher

than that of the cold-rolled or mechanical surfaces that usually form the basis for protective electrodeposits. This remark should not be misunderstood. The surface of the specimens was typical of that of hot-rolled steel, $\frac{3}{8}$ in. thick. The point is that electrodeposits are not commonly applied to this class of material, which is representative of heavy structural steel. This rough surface may have affected the porosity of the deposits and hence their protective properties, particularly in the case of cathodic metals.

(ii) The specimens plated at the Armament Research Department, Woolwich, were first degreased in trichlorethylene vapour and pickled for about 2 hr. in cold concentrated hydrochloric acid containing antimony oxide as an inhibitor (20 g./litre). After rinsing, they were scrubbed vigorously with a stiff bristle brush loaded with pumice powder and water. This was followed by alternate anodic and cathodic treatments in sulphuric acid (25% by weight) at a current density of 200 amp./sq. ft. until the surface was uniformly light grey in colour and free from local patches of scale. After rinsing to remove the sulphuric acid, the cleaned specimens were dried off with boiling water, cooled, and weighed. Immediately before plating, the specimens were given a short cathodic treatment at 50 amp./sq. ft. in a solution of 5% sodium hydroxide + 5% sodium carbonate, followed by a light scrub with pumice and a rinse in water. This final treatment was necessary in order to ensure good adhesion of the deposits; it did not materially affect the weights of the specimens.

In order to secure coatings of uniform thickness, the following procedure was adopted: Each specimen was plated singly in a rectangular glass cell, 12 × 9 × 18 in. deep, and it occupied almost the entire vertical cross-section of the solution. The anodes were approximately the same size as the specimen (15 × 10 in.) and one anode was suspended on either side of the specimen, parallel to it and 3½ in. from it. After plating, the specimens were thoroughly rinsed and dried off with hot water.

The degree of uniformity obtained under these operating conditions was checked by making local thickness determinations by means of the B.N.F. jet test ¹³ on trial specimens of zinc and cadmium. Thirty-one individual determinations were made on each face and a summary of the results is given in Table X. In addition, the coating thickness was checked at several points on a trial lead-plated specimen by chemical analysis of pieces cut from it; the results were found to be satisfactorily uniform.

(iii) In the case of zinc and cadmium, two of the specimens that had been plated from a cyanide bath were immersed for 2 min. in a solu-

* Shot-blasting may be used when convenient, and degreasing is sufficient for bright steel articles.

TABLE VII.—*Analysis of the Metals and Alloys Used in the Coating Processes.*

Metal or Alloy and Coating Process.	Analysis, %.	Notes.
(1) <i>Aluminium.</i>		
(1.7) Sprayed, molten-metal pistol.	Si 0.5 Fe 0.4 Cu 0.02 Mn 0.02 Mg 0.01 Ti 0.01	Good commercial purity.
(1.8) Sprayed, powder pistol.	Cu 3.3 Fe 0.4 Mn 0.3 Si 0.3 Mg 0.1 Ni 0.1 Ti 0.01	Presumably made from secondary material. The presence of Cu 3.3% is likely to affect adversely the corrosion resistance of the coating.
(1.9) Sprayed, wire pistol.	Fe 0.25 Si 0.12 Mg <0.01 Mn 0.01 Ti 0.01 Cu 0.006 Ni not detected.	Good commercial purity.
(2) <i>Cadmium.</i>		
(2.7) Sprayed, molten-metal pistol.	Cd 99.95–100.00	
(2.8) Sprayed, powder pistol.	Sn, Pb, Cu and Fe present.	Spectrographic analyses. Standards not available, but sample is of reasonably high purity.
(2.9) Sprayed, wire pistol.	Pb, Cu present, Sn, Zn trace.	As for (2.8).
(3) <i>Cadmium–Zinc (82/18) Alloy.</i>		
(3.7) Sprayed, molten-metal pistol.	Cd 82.3 Pb 0.35 Sn 0.72 Zn 16.6 (by difference)	The Sn content is higher than desirable; the presence of tin in zinc coatings may lead to pitting under certain conditions.
(3.8) Sprayed, powder pistol.	Cd 80.7 Zn 19.2 Pb 0.04 Sn 0.03	Zn determined by difference. Good commercial grade.
(4) <i>Zinc.</i>		
(4.0) Cemented (sherardized).	Pb 0.16 Cd 0.15 Cu 0.0005 Sn trace	Good commercial grade of zinc dust.
(4.4) Hot-dipped (Firm A).	Pb 0.724 Fe 0.042 Cd trace Sn nil	
(4.5) Hot-dipped (Firm B).	Pb 1.4 Sn 0.41 Cd 0.13 Cu 0.03	As for (3.7).
(4.7) Sprayed, molten-metal pistol.	Zn 99.997	High-purity zinc.
(4.8) Sprayed, powder pistol.	Pb 0.90 Cd 0.19 Sn c. 0.02 Cu 0.005	Good commercial grade.

TABLE VII.—*Continued.*

Metal or Alloy and Coating Process.	Analysis, %.	Notes.
(4) <i>Zinc</i> —Continued. (4.9) Sprayed, wire pistol.	Pb c. 0.01 Cd 0.002 Fe <0.001 Cu c. 0.0005	High-purity zinc.
(5) <i>Lead</i> . (5.4) Hot-dipped.	Sn 1.99 Bi 0.008 Cd 0.002 Cu 0.001 Ag 0.0001 As, Sb, Hg, Ni, Fe, Zn not detected.	The tin was added to promote wetting of the steel surface.
(5.7) Sprayed, molten-metal pistol.	Sb 0.004 Bi 0.0011 Fe, As, S 0.00052 Cu 0.0003 Zn 0.0003 Ag 0.0002 Cd 0.0001 Sn nil	
(5.8) Sprayed, powder pistol.	Sn 0.01 Cd 0.005 Sb 0.005 Cu 0.002 Bi 0.001 Ag 0.0002 As, Hg, Ni, Fe, Zn not detected.	
(5.9) Sprayed, wire pistol.	Sb 0.34 Cu 0.04 Cd 0.002 Bi 0.0005 Ag 0.0002 As, Hg, Ni, Fe, Sn, Zn not detected.	
(6) <i>Lead-Tin</i> (88/12) <i>Alloy</i> . (6.4) Hot-dipped.	Sn 12.50 Cd 0.1 Cu 0.05 Bi 0.01 Zn c. 0.0001 Al not detected.	Commercial purity.
(6.7) Sprayed, molten-metal pistol.	Sn 12.51 Cd 0.1 Cu 0.1 Bi 0.01 Zn c. 0.001 Al not detected.	Commercial purity.
(6.8) Sprayed, powder pistol.	Sn 14.21 Cd >0.1 Cu 0.05 Bi 0.004 Zn c. 0.001 Al not detected.	Commercial purity.
(7) <i>Tin</i> . (7.4) Hot-dipped.	As <0.01 Pb 0.01 Bi 0.001 Cu 0.001 Sb <0.008 Ag 0.0003	Pure tin, probably of higher purity than would normally be used for hot-tinning.

TABLE VII.—*Continued.*

Metal or Alloy and Coating Process.	Analysis, %.	Notes.
(7) <i>Tin</i> —Continued.		
(7.7) Sprayed, molten-metal pistol.	Pb 0.052 Sb 0.030 Cu 0.025 Bi 0.020 As 0.016 Co 0.008 Fe 0.007 Ag 0.001	Commercial purity.
(7.8) Sprayed, powder pistol.	Bi 0.1 Pb 0.1 Zn 0.02 As 0.01 Sb 0.008 Cu 0.005 Ag <0.001 Cd 0.001 Al not detected.	Commercial purity.

A few of these figures represent analyses made in the works using the process, or are figures stated by the smelters. The majority, however, are the results of analyses made by the British Non-Ferrous Metals Research Association; most of these analyses were spectrographic, although some chemical determinations of metals present in appreciable amounts were made.

TABLE VIII.—*Composition of Plating Solutions.*

	Grammes per litre.*
(a) <i>Zinc Solution (Acid Type).</i>	
Zinc sulphate. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	360
Ammonium chloride. NH_4Cl	30
Sodium acetate. CH_3COONa	15
Glucose (B.P.)	120
(b) <i>Zinc Solution (Cyanide Type).</i>	
Zinc oxide. ZnO	45
Sodium cyanide. NaCN	75
Caustic soda. NaOH	15
(c) <i>Cadmium Solution.</i>	
Cadmium oxide. CdO	29
Sodium cyanide. NaCN	54.8
(f) <i>Lead (Perchlorate) Solution.</i>	
Litharge. PbO	320
Perchloric acid. HClO_4 (60% technical)	570
Peptone (bacteriological)	2.5
(g) <i>Tin (Sodium Stannate) Solution.</i> †	
Sodium stannate. $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$. .	56
Caustic soda. NaOH	12

* The quantities given should be made up to 1 litre with distilled water.

† Further information on the methods of making up and working the sodium stannate bath will be found in "Electro-Tinning," by S. W. Baier, *Publication No. 92*. Greenford, Middlesex: 1939.

tion of 1% chromic acid + 0.1% sulphuric acid at 18° C.‡ On removal they were rinsed in cold water, swabbed off, and allowed to dry in a current of air. This treatment ensures complete removal

‡ There was an interval of several weeks between electrodeposition and the chromate treatment.

of any plating salts left on the coating, and also produces a thin chromate film on the surface.

The chromate film on the cadmium-plated specimens appeared to be thicker and more adherent than that on the zinc-plated specimens; the plated zinc deposit was not so smooth as the

TABLE IX.—*Conditions of Electrodeposition.*

Deposit.		Bath Temp., ° C.	Current Density, amp./sq. ft.	Plating Time.	
Metal.	Thick-ness, mils.			Hr.	Min.
(a) Zinc (acid bath)	3	18	6.0	7	30
(b) Zinc (cyanide bath)	1	30	4.5	3	0
	3	30	2.4	16	40
	5	30	4.1	16	40
(d) Cadmium	1	30	3.2	3	4
	3	30	3.9	7	30
	5	30	2.9	16	40
(f) Lead	1	18	9.5	0	45
	3	18	9.5	2	15
	5	18	9.5	3	45
(g) Tin	3	76–80	15	3	30
	5	76–80	15	6	5

cadmium, and this may account for the difference.

(iv) In the case of lead electrodeposited from a perchlorate bath, it was found necessary, in order to prevent blistering of the deposits, to give the specimens a final anodic treatment in sulphuric

TABLE X.—*Local Variation in Thickness of Electrodeposited Zinc and Cadmium Coatings.*

Deposit,		Deviation from Average Thickness, %.*			
		Face A,		Face B,	
Metal,	Thickness, mils.	Limits,	Standard Deviation,	Limits,	Standard Deviation,
Zinc (acid bath) . . .	1.0	+14.8 to -8.7	5.7	+11.6 to -9.7	5.4
Cadmium	0.5	+11.5 to -7.7	5.8	+8.6 to -8.6	5.1

* Thirty-one readings were taken on each face, using the B.N.F. Jet Test. Eight readings taken $\frac{1}{2}$ in. from the edge have been excluded from these results.

It will be noted that, except for readings near the edge, the average standard deviation is 5.5%, which is regarded as satisfactory. On the whole the electrodeposited coatings as prepared for these tests were the most uniform in thickness of the metallic coatings.

acid immediately before plating, instead of the cathodic treatment in alkali. This caused a loss in weight due to anodic dissolution, and a correction was applied to the weight of coating. This correction was determined by tests on spare specimens, and varied from 5 to 7 g. according to the duration of the final anodic treatment.

(v) The specimens electroplated with tin at the Tin Research Institute were first descaled by pickling in cold 30% (by volume) hydrochloric acid, rinsed, dried, and weighed. Immediately before plating they were treated cathodically for 30 sec. in 5% caustic soda solution at 90° C. at a current density of 80–90 amp./sq. ft. They were then placed in cold 30% hydrochloric acid for about 30 sec., rinsed in water, and given a final treatment in the caustic soda bath for about 30 sec., being made alternately anodic and cathodic in rapid succession. After a rinse in water, the specimens were placed in the plating solution. The plating bath was 24 × 18 × 18 in. Two specimens were plated at the same time, being suspended from a central brass rod placed between two similar rods, each carrying two pure-tin anodes. The four anodes were approximately the same size as the specimens (15 × 10 in.) and were placed about 4 in. from them. At the commencement of plating the two specimens were placed in the solution and connected to the cathodic bus-bar; the anodes were then connected and lowered into the solution with the plating current already switched on. This procedure causes an oxidized film to form on the surface of the tin anodes and ensures that the tin goes into solution in the quadrivalent state.

(e) *Hot-Dipped Coatings.*

Coatings of aluminium, zinc, lead, lead-tin (88/12) alloy, and tin, were applied to specimens by hot-dipping. Some of the aluminium-coated specimens were subsequently heat-treated.

(i) *Aluminium, Hot-Dipped (1.4).*

This process, sometimes called wet-calorizing, is applied primarily to reduce the scaling of steel at moderately high temperatures. As in the case of the usual (dry) calorizing, no claim is made that the coating is especially resistant to corrosion in the atmosphere.

The specimens were shot-blasted, pickled for 20 min. in cold 20% (by volume) hydrochloric acid, rinsed in water, then in calcium chloride solution, and allowed to dry. The calcium chloride acts as a flux. After weighing, the specimens were immersed in a bath of molten aluminium for 12 min. On removal they were allowed to drain, and the excess aluminium was quickly scraped off.

The coating was smooth, light greyish-white in colour for the most part, though appreciably discoloured by darker spots. There was some metallic lustre at the edges. On most specimens there was an accumulation of metal near one corner, due to drainage on removal from the bath.

Some of the specimens prepared as above were given an annealing treatment designed to promote alloying of the aluminium coating with the basis steel. Details of the treatment were not divulged.

(ii) *Zinc, Hot-Dipped (Firm A) (4.4).*

The hot-galvanized specimens were prepared by hand-dipping. First, they were descaled by pickling in cold 12% hydrochloric acid, rinsed in water, dried, and weighed; then they were given a quick fluxing dip in the pickling bath and placed on the side of the galvanizing bath to dry before dipping. The galvanizing bath was a large one containing 120 tons of zinc. It was fiddle- or banjo-shaped, 25 ft. 6 in. long by 5 ft. wide for 13 ft. of its length, and 2 ft. 6 in. wide for the remainder; the depth of molten zinc was 5 ft. The bath was coke-fired, and its temperature was kept at 830–835° F. (443–446° C.).

The specimens were dipped singly at the narrow

end of the bath. When thoroughly dry and warm, they were suspended from one corner on a wire and dipped quickly into the zinc through a layer of flux (zinc ammonium chloride). "Boiling-off"—i.e., the action of the flux in cleaning the surface of the steel—commenced as soon as the specimen was immersed, became most vigorous after 10–15 sec., and ceased after about 30–50 sec. The specimens requiring a thin coating were lifted out of the bath slowly and steadily as soon as "boiling-off" ceased, the total time of immersion being about 50 sec. Those requiring medium coatings were immersed for 75–85 sec. and those requiring thick coatings for $3\frac{1}{4}$ – $3\frac{1}{2}$ min. After withdrawal, the specimens were allowed to drain for a few seconds, shaken to remove any excess of zinc from the suspension holes, and plunged into cold water to wash-off the flux.

The composition of the bath is given in Table VII.

The coated specimens had a bright, smooth, light-grey surface, with no marked spangles. There was generally a slight accumulation of zinc near the corner that had been at the bottom when dipping the specimen, and there were slight tarnish marks diagonally across the surface caused by the flux when withdrawing the specimen.

(iii) *Zinc, Hot-Dipped (Firm B) (4.5).*

In view of the wide industrial use of hot-galvanizing, it was thought advisable to duplicate the tests on this type of coating. Accordingly, arrangements were made for a small number of specimens to be hot-galvanized by another firm. In this case the general procedure of the hot-dipping process was essentially the same as that already described, except that the galvanizing bath was smaller, measuring 12 ft. 6 in. by 5 ft. deep (Fig. 15). The temperature of the bath was 430° C. and for a coating of medium thickness the specimens were immersed for approximately 2 min.

The composition of the bath is given in Table VII.

The appearance of the coatings resembled that of the other hot-galvanized coatings but the surface markings caused by the flux were more noticeable.

(iv) *Lead, Hot-Dipped (5.4); Lead-Tin (88/12) Alloy, Hot-Dipped (6.4); and Tin, Hot-Dipped (7.4).*

These coatings were applied at the Tin Research Institute by arrangement of Dr. E. S. Hedges and Mr. W. E. Hoare. In all three cases the procedure up to the point of dipping was the same, namely, that the specimens were descaled by pickling for about 10 min. in 10% sulphuric acid at 85° C., rinsed in water, dried, and weighed. They were then redipped for 30 sec. in the pickling bath to remove any tarnish film, rinsed in water, swabbed

with concentrated zinc ammonium chloride solution and finally immersed singly in the bath of molten metal.

The pot used for the hot-dipping was 13 in. long, 6 in. wide, and 20 in. deep (see Fig. 16). It had a shallow partition, extending 6 in. down from the top, dividing the surface into two parts, $1\frac{1}{2}$ and $4\frac{1}{2}$ in. wide, respectively. This made it possible to cover part of the molten metal with flux, whilst leaving the other part clear or covering it with oil as desired.

The compositions of the coating baths are given in Table VII. The lead used contained 2% of tin; this was deliberately added to promote wetting of the steel by the lead and thus facilitate the production of satisfactory coatings. The tin content of the lead-tin alloy, nominally 12%, was chosen as representative of commercial alloys used forterne plate.

The lead bath was kept at a temperature of 380° C. and the specimens were immersed in it for approximately 3 or 4 min. until a complete coating was obtained. In this case and also in that of the lead-tin alloy, owing to the high density of the metal, it was necessary to push the specimens under the surface. The specimens were removed through the flux, allowed to drain for a few minutes and finally plunged into cold water whilst still hot to wash off the flux.

In the case of the lead-tin alloy coatings, the procedure was exactly the same, except that the bath was at a temperature of 360° C.

For the production of hot-dipped tin coatings, a little ammonium chloride was added to the zinc chloride flux covering the bath. The specimens were immersed for 2 or 3 min. at a temperature of 270° C. and withdrawn through the flux (Fig. 16). As the resultant coating was not considered entirely satisfactory, each specimen was subsequently re-dipped at a temperature of 250° C. for approximately 4 min., being immersed and withdrawn through a surface kept clean by tallow. On removal, the specimens were allowed to drain and were cooled in air. A slight tarnish film formed on the coating; this was removed by dipping for about 5 sec. in 5% caustic soda solution at 80° C.

The specimens coated with tin were a smooth white with a mirror finish, and those coated with lead or lead-tin alloy had a smooth, dark-grey surface. There were a few small pin-holes in parts of the lead coating but none in the lead-tin alloy coating, and in the case of all three sets of specimens there were slight accumulations of coating metal along the edge that had been at the bottom when dipping.

(f) *Coatings Sprayed by the Molten-Metal Pistol.*

Sprayed coatings of the seven metals or alloys investigated, namely, aluminium, cadmium, cad-

mium-zinc (82/18) alloy, zinc, lead, lead-tin (88/12) alloy, and tin, were applied to specimens by the molten-metal pistol.

(i) *General Description of the Molten-Metal Pistol.*

In the molten-metal spraying process, the metal is melted separately in a crucible furnace and ladled into the pistol as required. The metal reservoir of the pistol is heated by gas to keep the metal molten. The metal flows under gravity to a hardened steel nozzle where it is atomized and sprayed by a heated air blast. Owing to the gravity feed the pistol is designed to operate in a slightly downwards direction; a modified form can be used in an upwards direction. The pistol uses coal gas at mains pressure and compressed air. It has no moving parts.

The standard pistol holds approximately 4 lb. of zinc; this is sufficient for about 20 minutes' operation. Naturally the rate of application varies with the shape and size of the article being sprayed, but as an average figure, it may be taken that zinc can be deposited to a nominal thickness of 4 mils at a rate of 80 sq. ft./hr., including stoppages.

Tin, lead, and cadmium can be sprayed by the standard pistol, as used for zinc.

For aluminium a modified form of pistol is used, because the melting point of aluminium (658° C.) is considerably higher than that of zinc (419° C.). This necessitates heating the container to a higher temperature and cooling the operator's handle by compressed air. Molten aluminium readily oxidizes in air, with the result that trouble may be caused by particles of aluminium oxide blocking the nozzle when the pistol is used intermittently. Owing to the higher temperature, the nozzle on the aluminium-spraying pistol wears much more rapidly than that on the standard one.

(ii) *Preparation of the Specimens.*

The specimens were first descaled by shot-blasting, this being a necessary treatment of metal surfaces before spraying by any process. After weighing, the specimens were sprayed with the desired metal. In operation the pistol was held about 6 in. from the work, and each surface was gone over at least twice in two directions at right-angles. Each stroke of the pistol sprays a band about $\frac{3}{4}$ in. wide; the strokes in each direction overlap and repetition of the process at right-angles leads to a fairly uniform coating. Coatings of various thicknesses were applied. The thin coatings, specified as 1 mil thick, were applied in two quick passes and the thick ones, specified as 5 mils thick, in two slower passes.

This general description is applicable to all the coatings and it is unnecessary to refer to each in detail, apart from noting the following points:

(iii) *Composition of Metals and Alloys Used.*

Details of the composition are given in Table VII., but the salient features are as follows:

Aluminium (1.7)	99% pure.
Cadmium (2.7)	99.95% pure.
Cadmium-zinc alloy (3.7)	82% cadmium; 1% impurities. Nominally 82/18 to correspond with the eutectic alloy.
Zinc (4.7)	99.997% pure.
Lead (5.7)	99.99% pure.
Lead-tin alloy (6.7)	12.5% tin; 0.2% impurities. Nominally 88/12 to correspond with the hot-dipped alloy coating ("terne").
Tin (7.7)	99.8% pure.

(iv) *Appearance of Coatings.*

All the coatings had a smooth, mat, metallic surface. The colour of the coatings varied in darkness as follows:

White:	Aluminium and tin alloy.
Light grey:	Cadmium, cadmium-zinc (82/18) alloy, and zinc.
Grey:	Lead-tin (88/12) alloy.
Dark grey (with slight discolouration):	Lead.

(v) *Lead and Lead-Tin (88/12) Alloy Coatings.*

Owing to the danger of lead poisoning, the spraying of these two coatings was carried out in well-ventilated shops by operators wearing helmets fed with fresh air. Some difficulty was experienced owing to the development on the lead coatings a few hours after spraying of brown or black surface markings, presumably due to lead sulphide. This was minimized by spraying at as low a temperature as possible. No discolouration occurred in the case of the lead-tin alloy coating.

(g) *Coatings Sprayed by the Powder Pistol.*

Coatings of the seven coating metals or alloys tested were also applied to specimens by means of the powder pistol.

(i) *General Description of the Powder Pistol.*

The powder pistol uses metal in the form of powder passed through a 150-mesh sieve; for zinc-spraying, dust or "fines" of 200-300 mesh is sometimes used, this material being available at low cost as a smelting by-product. The powder is placed in a special container, from which it is sucked to the pistol as a suspension in an air stream. The necessary suction is created in the pistol by compressed air at a Venturi-type jet and is controlled by the operator's thumb, which is placed over a small hole connecting the powder intake to the atmosphere. The metal powder is ejected from the pistol by compressed air through an oxy-fuel-gas flame on to the surface being sprayed, being fused in passing through the flame. The pistol is light and easily handled, and spraying

can be done in any direction. It uses compressed air, oxygen, and a fuel gas such as acetylene, propane, or enriched coal-gas. There are no moving parts.

The special powder container is shaped like an egg-timer or hour-glass. The powder, which must be freshly sieved and very dry, flows from one compartment into the other, being aspirated to the pistol from the centre portion as it falls. To maintain the flow of powder, the container is vibrated by a small air turbine. The container is turned upside down at intervals as required.

The powder pistol can be used for spraying tin, lead, zinc, cadmium, aluminium, copper, or various alloys of these metals, provided that they are in the form of powder. The rate of application naturally varies with the shape and size of the article being sprayed but as an average figure, it may be taken that zinc can be deposited to a nominal thickness of 4 mils at a rate of 100 sq. ft./hr., including stoppages; when working on flat surfaces, rates considerably in excess of this figure can be achieved.

(ii) *Preparation of the Specimens.*

The specimens were descaled by shot-blasting and, after they had been weighed, were sprayed with the desired metal. In operation the pistol was held 8–10 in. from the work and each surface was gone over at least twice in two directions at right-angles. Each stroke of the pistol sprays a band about $\frac{3}{4}$ in. wide; the strokes in one direction overlap and by repeating the process at right-angles a fairly uniform coating is obtained. All the spraying was conducted in front of a fan in a well-ventilated shop.

(iii) *Composition of Metals and Alloys Used.*

Analyses of the metallic powders used for spraying are given in Table VII. from which the following facts will be noted :

Aluminium (1·8)	95·5% pure; presumably made from secondary material. The presence of 3·3% of copper would probably affect the corrosion resistance adversely.
Cadmium (2·8)	Of reasonably high purity.
Cadmium–zinc alloy (3·8)	80% cadmium, 19% zinc. Nominally 82/18 to correspond with the eutectic alloy used for the molten-metal pistol.
Zinc (4·8)	99% pure.
Lead (5·8)	99·98% lead.
Lead–tin alloy (6·8)	86% lead, 14% tin. Nominally 88/12 to correspond with the hot-dipped alloy (“terne”) and the coating applied by the molten-metal pistol.
Tin (7·8)	99·8% tin.

(iv) *Appearance of Coatings.*

All the coatings had a smooth mat metallic surface, the colour increasing in darkness from

white to grey in the same order as already noted for the coatings applied by the molten-metal pistol. Some of the surfaces sprayed with cadmium or cadmium–zinc alloy were slightly tarnished or stained locally by a yellowish-brown film, presumably of cadmium oxide or sulphide.

(h) *Coatings Sprayed by the Wire Pistol.*

Coatings of aluminium, cadmium, zinc, and lead were applied by the wire-spraying process.

(i) *General Description of the Wire Pistol.*

The wire pistol uses wire, generally of 1, $1\frac{1}{2}$, or 2 mm. in dia., which is led to the pistol from a freely rotating reel. Thicker wires are occasionally used but require special nozzles, otherwise the texture of the sprayed metal tends to be coarser. Inside the pistol a small geared turbine driven by compressed air operates rollers, which pull the wire from the reel and drive it into the interior of an oxy-fuel-gas flame. The speed of the turbine is adjusted in relation to the size and temperature of the flame, so that the wire is melted continuously as it is fed into the flame. The molten droplets of metal then encounter an air blast, which atomizes and sprays the metal.

The pistol is light and easily handled, and spraying can be done in any direction; special nozzles are available for spraying the inside of pipes and other intricate work. The pistol uses compressed air, oxygen, and a fuel gas such as acetylene, hydrogen, propane, or compressed coal gas. Wear of the gears is minimized by running them in a grease bath, but the moving parts require attention at intervals.

The wire pistol can be used for spraying tin, lead, zinc, cadmium, aluminium, copper, nickel, steel, and various alloys, provided that they can be drawn into wire and that their melting points do not exceed 1500–1600° C. The rate of application naturally varies with the shape and size of the article being sprayed, but as an average figure, it may be taken that, using 1-mm. dia. wire, zinc can be deposited to a nominal thickness of 4 mils at a rate of 20 sq. ft./hr., including stoppages; this rate can be increased to 80 sq. ft./hr. by the use of 2-mm. dia. wire, together with a suitable fuel gas.

(ii) *Preparation of the Specimens.*

As in the case of the other metal-spraying processes, the specimens were descaled by shot-blasting and then weighed before spraying with the desired metal. In operation, the pistol was held about 4 in. from the work and each surface was gone over at least twice in two directions at right-angles. Each stroke of the pistol sprays a band about $\frac{1}{2}$ in. wide; the strokes in each direction overlap to some extent and the repetition of the

process at right-angles leads to a fairly uniform coating. The spraying of cadmium and lead was conducted in a special chamber fitted with a suitable exhaust.

(iii) *Composition of Metals Used.*

Analysis of the wires used (Table VII.) showed that the essential composition of the metals was as follows :

Aluminium (1.9)	99.6% aluminium.
Cadmium (2.9)	Of reasonably high purity.
Zinc (4.9)	99.99% zinc.
Lead (5.9)	99.6% lead, 0.3% antimony.

(iv) *Appearance of Coatings.*

All the coatings had a smooth mat metallic surface, *viz.*, white for aluminium and cadmium, light grey for zinc, and dark grey for lead. The lead coatings were considerably tarnished by a dark brown film, presumably of lead sulphide.

(i) *Composite Protective Schemes (Metallic Coatings plus Paint).*

A set of specimens was included in the atmospheric-exposure tests in which the protective treatment consisted of two coats of red oxide in linseed-oil paint applied over each of the following ten metallic coatings :

Aluminium, cemented.	The normal coating (1.02).
Aluminium, sprayed by the wire pistol.	Thin (1.91) and medium (1.92) coatings.
Zinc, cemented.	The normal coating (4.01).
Zinc, hot-dipped.	Thin (4.41) and medium (4.42) coatings.
Zinc, sprayed by the wire pistol.	Thin (4.91) and medium (4.92) coatings.
Lead, electrodeposited.	Thin (5.11) and medium (5.12) coatings.

The metallic coatings were applied to the specimens in the manner described in previous sections. The nominal thicknesses of thin and medium coatings were 1 and 3 mils, respectively, but marked deviations occurred from these figures. The hot-dipped zinc specimens were etched with the following solution before painting :

Commercial hydrochloric acid	5 parts by volume.
Carbon tetrachloride	5 " "
Toluol	30 " "
Denatured alcohol	60 " "

The solution was applied with a clean brush and, when dry, the surface was wiped over with a clean rag.

In the case of the specimens coated with electrodeposited lead, one of each pair was treated with a wash consisting of a 35% (by weight) solution of phosphoric acid (sp. gr. 1.70) in methy-

lated spirit (61 O.P.). This was applied by brush, allowed to dry for $\frac{1}{2}$ hr., and washed off with clean water; the priming coat of paint was applied as soon as the specimens had dried again.

With these two exceptions, the paint was applied directly over the metallic coating without any preliminary surface treatment. The control specimens, carrying two coats of the same paint but no metallic coating, were prepared for painting by treatment at a works where the sulphuric-acid/phosphoric-acid pickling process, developed by Footner,¹⁴ is in operation on a large scale. They were descaled by immersion for 15–20 min. in dilute (5–10%) sulphuric acid at 60–65° C., rinsed in hot water at 60–65° C., and finally immersed for 3–5 min. in a bath containing approximately 2% of free phosphoric acid and 0.3–0.5% of iron, heated to 85–90° C.* On removal from the final bath the specimens dried rapidly, leaving a dull grey film of iron phosphate on the surface. This film by itself has little protective value but forms an excellent basis for paint.†

Red oxide paint was used and had the following composition :

Natural Spanish iron oxide, %	62
Refined linseed oil, %	21
Boiled linseed oil, %	12
White spirit, %	2
Driers, %	3

In all cases the paint was applied by brush in the laboratory, allowing ample drying time between coats and before exposure. The total weights of dry paint on each specimen are given in Table IV.; it will be seen that the sprayed-metal surfaces required slightly more paint than the relatively smooth, hot-dipped or electroplated specimens, while the cemented aluminium coatings required considerably more.

APPENDIX B.—*Laboratory Examination of the Coated Specimens.*

Each coated specimen was examined in a standard manner in the laboratory before exposure. In addition, specimens representative of each type of coating and prepared for the purpose at the same time as the others, were subjected to a more thorough examination involving the use of destructive methods.

(a) *Standard Examination of All Coated Specimens.*

The method of examination adopted for all specimens sent out for exposure test included (a) weighing, (b) visual inspection of the surface, and (c) determination of the coating thickness.

(i) *Weighing.*—The weights of the coated specimens were recorded to the nearest 0.01 g., the

* The figures given are typical of operating conditions for this process.

† To get the best results from the process, the pickled parts should be painted immediately they are dry, while they are still warm. In the case of the specimens some delay occurred before painting, but they were carefully stored during the interval.

probable accuracy of a determination being ± 0.03 g. The weight of coating in each case was deduced by differences from the final weight and the weight after the preliminary descaling or other treatment. The latter weighing was, as already mentioned, made in the works concerned on a balance belonging to the Committee; with this balance weighings were made to the nearest 0.5 g., so that the coating weight is correct to about this amount.

(ii) *Surface Inspection*.—The appearance of the coating was recorded and the positions of any marks or defects noted.

(iii) *Coating Thickness*.—The thickness of all the metallic coatings was measured on both faces of each specimen by means of a commercial model of the electromagnetic thickness meter, described

hard-chromium deposit. The readings on these surfaces remained constant, showing that the meter was giving consistent readings.

Each of the figures for the coating thickness (T_m) given in Table II. and elsewhere is the average of the twenty-four meter readings taken on the front and back of each specimen. In general, this value varied in proportion to the weight of the coating, as is illustrated in Fig. 24, which is a typical result. This shows the mean coating-thickness plotted against the weight of coating, for the forty specimens zinc-sprayed by the wire pistol. It will be seen that the points lie close to a straight line which intersects the coating-thickness axis near the origin. Similar graphs have been drawn for other coatings. In most cases the intercept on the coating-thickness axis

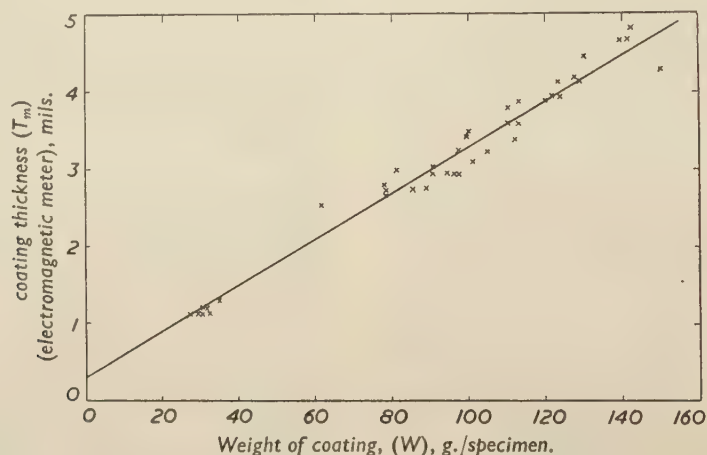


FIG. 24.—Correlation between Mean Coating Thickness (Electromagnetic Meter) and Weight of Coating. (The points refer to 40 specimens sprayed with zinc by the wire pistol.)

by Chalmers, Hoare, and Tait,¹⁵ which measures the thickness of non-magnetic coatings on an iron or steel base. Readings were taken with the meter at twelve positions on each surface. These positions were spaced regularly in four rows of three, and were located by placing on the specimen a plywood template with holes into which the exploring head of the meter was inserted. In order to avoid scratching any of the coatings with the exploring head, all readings were taken with a thin sheet of cellophane over the specimens. A correction for the error introduced in this way was determined by taking thickness readings both with and without the cellophane on specimens specially reserved for this purpose. The error was about 0.7 mil and varied slightly for different metals. When in use, the meter was checked frequently by taking readings on mild-steel discs plated with copper, followed by a thin

lies between 0 and 0.5 mil, which may be accepted as a satisfactory zero error for the instrument. The intercepts for the various types of cadmium coating were outside this limit, however, being about 1 mil or more; presumably the calibration of the meter in respect of this metal was at fault to some extent.*

In the course of this work, over 10,000 individual thickness determinations were made. Apart from their direct use in calculating the average coating thickness on each specimen, the results are of value in defining the magnitude of the local variations in thickness that are liable to occur in the various types of coating. It would be an interesting mathematical exercise to make a statistical analysis of the results, but it is doubtful whether this would repay the time and labour involved. The magnitude of the variations observed will be illustrated sufficiently well for the

* The meter is calibrated for the various coating metals by the suppliers; this is done by taking readings on coatings of known thickness, measured by a micrometer. The absolute values of thickness readings for any particular metal are generally correct to about 10%.

purposes of this report by the data presented in Table XI. for single specimens, selected at random, coated with zinc by each of the eight processes used for the application of this metal. It would be invidious to make comparisons between the individual processes on the basis of these snap results but, as a general conclusion, it may be stated that variations from the average thickness of up to some 30% occurred in the case of the test-specimens, which are of comparatively simple shape. Obviously much greater differences are to be expected in the case of articles of more complicated shape, such as are coated in the general run of industry.

It may be added that the authors' experience with this type of thickness meter to date leads them to believe that, while reliable, comparative

(b) Porosity tests of several types.

(c) Microscopic examination of sections through the coatings.

(d) Determination of the density of the sprayed coatings.

In addition, the adhesion of some of the coatings was tested by means of an instrument devised for picking out non-adherent thin electrodeposits¹⁶ but none of the relatively thicker coatings on the present specimens broke down under this test.

(i) *Measurement of Coating Weight by Stripping.*

A known area (about one-quarter, or in some cases one-sixteenth) was cut from the specimen and weighed. The coating was then stripped as described below and the mean coating weight of

TABLE XI.—*Local Variation in Thickness of Zinc Coatings.*

(These figures are for isolated specimens selected at random and in any particular case may not be truly representative of the process as a whole.)

Method of Application.	Coating Thickness, mils.						
	Average.*			Range.			
				Front.		Back.	
	Front.	Back.	Mean.	Min.	Max.	Min.	Max.
(4.01) Cemented	1.36	1.23	1.30	1.1	(2.6) †	1.1	1.4
(4.12) Electrodeposited, sulphate bath	2.91	3.19	3.05	2.5	3.1	2.7	3.5
(4.22) Electrodeposited, cyanide bath	2.89	3.08	2.99	2.5	3.3	2.8	3.5
(4.42) Hot-dipped (Firm A)	2.79	2.71	2.75	2.5	3.1	2.3	3.3
(4.52) Hot-dipped (Firm B)	2.78	2.70	2.74	2.5	3.2	2.3	2.9
(4.72) Sprayed, molten-metal pistol	2.37	1.90	2.14	1.9	3.1	1.5	2.6
(4.82) Sprayed, powder pistol	6.12	4.19	5.16	4.6	8.0	3.2	5.3
(4.92) Sprayed, wire pistol	2.94	3.09	3.02	2.5	3.4	2.7	3.5

* Twelve readings were taken on each face, using the electromagnetic meter. The nominal coating thickness was 3 mils in all cases except that of the cemented zinc (sherardized) coating.

† This value is abnormal.

values can be obtained for the thickness of coatings of the same metal applied by similar processes, within the accuracy claimed by the makers ($\pm 10\%$), comparisons between coatings of different metals or even of the same metal applied by dissimilar processes should be made with caution, owing to the possibility of errors in the absolute thickness values.

(b) *Detailed Examination of Individual Coatings.*

A detailed examination of ninety of the metal-coated specimens, selected as representative, was made by the British Non-Ferrous Metals Research Association through the kind arrangement of Dr. H. Moore, C.B.E., and Mr. E. A. G. Liddiard. This included the following destructive tests:

(a) Measurement of coating weight by chemical and electrolytic stripping.

the portion of the specimen concerned was calculated from the observed loss in weight.

Aluminium Coatings.—A 25% caustic soda solution proved suitable for stripping the sprayed aluminium coatings and good agreement was observed between the loss in weight on stripping and the gain in weight on coating. This solution did not dissolve the iron-aluminium alloy formed on the cemented or hot-dipped specimens and in these cases the agreement was poor. The figures indicated that the cemented aluminium coating contained roughly 15% of free aluminium, the remainder being alloyed. The hot-dipped aluminium coating contained about 30% of free aluminium; this figure was reduced to about 5% by the heat-treatment given to some of the specimens.

Cadmium, Cadmium-Zinc (82/18) Alloy, and Zinc Coatings.—Hydrochloric acid inhibited by

antimonious chloride was used for stripping these coatings. At first, only 1 g. of antimonious oxide was added to each litre of acid but as this proved insufficient and permitted some attack on the steel base, this quantity was later increased to 20 g./litre, as recommended by Clarke.¹⁷

It is essential to use an excess of this solution and to keep it well stirred when stripping specimens. In general, the coating weights determined in this way were slightly greater than the gains in weight on coating; this was possibly due to local variations in coating thickness, though the fact that the weights determined by stripping were the greater seems to indicate that the acid had attacked the steel base to some extent.

Electrolytic stripping tests by Britton's method¹⁸ were carried out on some of the zinc-coated specimens. In the case of the hot-galvanized coatings, these tests showed that the thinner coatings contained higher proportions of iron-zinc alloy. The total weights of zinc in the coatings deduced from the electrical readings agreed well with the gains in weight on coating.

Lead and Lead-Tin (88/12) Alloy Coatings.—The coatings of lead or lead-tin alloy were stripped in glacial acetic acid containing approximately 5% of hydrogen peroxide. The results agreed fairly well with the gains in weight on coating, the agreement being better for thin than for thick coatings.

Tin Coatings.—For stripping the tin-coated specimens the hydrochloric-acid/antimonious-oxide solution was first tried, but this proved unsatisfactory as it attacked the steel base to a marked extent. Anodic treatment in caustic soda solution was also found to be unsatisfactory. The method finally used was that of immersion in a boiling solution containing 80 g. of lead acetate and 135 g. of caustic soda per litre of water. The results using this solution agreed fairly well with the gain in weight on coating.

(ii) Porosity Tests.

Various porosity tests were carried out on nineteen of the coatings, including representative coatings of cadmium, cadmium-zinc (82/18) alloy, lead, lead-tin (88/12) alloy, and tin; no test was made on either aluminium or zinc coatings. The method of test varied according to the coating metal, as described below; all the specimens were given a cathodic degreasing treatment in sodium carbonate solution before the porosity test was made.

Cadmium and Cadmium-Zinc (82/18) Alloy Coatings.—These coatings were tested by the following two methods :

(1) The formation of bubbles in 1% hydrochloric acid after immersion for 10 min.

* Filter paper soaked in a solution containing potassium ferricyanide, 5 g./litre, and sodium chloride, 10 g./litre, and then dried.

† An uneven coating due to drainage. The porosity test-specimen was cut from the top of the specimen.

(2) The formation of blue spots when the specimen was made the anode in a solution containing 20 g. of potassium ferrocyanide in 50 c.c. of water, using a zinc cathode and applying a potential difference of 4 V.

Lead and Lead-Tin (88/12) Alloy Coatings.—A modified hot-water test, in which the specimen is immersed for 6 hr. in a solution containing 0.1 g. of sodium sulphate per litre of distilled water at 95° C., was applied to the lead and lead-tin alloy coatings; rust spots developed at the pores. An additional test was made on the lead coatings only. In this, the specimens were exposed to iodine vapour for 20 min.; as a result, drops of black liquid (ferric iodide) formed at the pores. A moistened sheet of ferroxyl paper * was applied to the surface immediately after exposure to the vapour; the pores were revealed by the development of blue spots on the paper.

Tin Coatings.—The tin-coated specimens were tested by immersion in distilled water at 95° C. for a period of 6 hr.; the positions of pores were indicated by rust spots.

Results.

The tests described are largely qualitative in character and vary for different groups of coating metal. Accordingly, comparisons of the various coatings as regards porosity should be made with reserve, but the general nature of the results obtained may be stated as follows :

(1) As would be expected, there was a marked tendency for the porosity of a given coating to decrease with increasing coating thickness.

(2) Of the nineteen coatings tested, the following were classified as (i) non-porous, (ii) negligibly porous, and (iii) appreciably porous :

(i) Non-Porous.

(6.41) Lead-tin (88/12) alloy, hot-dipped, 0.40 oz./sq. ft. (terne plate).

(ii) Negligibly Porous.

(5.13) Lead, electrodeposited, 4.79 oz./sq. ft.

(5.42) Lead, hot-dipped, 0.74 oz./sq. ft.

(7.22) Tin, electrodeposited, 1.78 oz./sq. ft.

(iii) Appreciably Porous.

(2.72) Cadmium, sprayed, molten-metal pistol, 1.56 oz./sq. ft.

(3.71) Cadmium-zinc (82/18) alloy, sprayed, molten-metal pistol, 0.46 oz./sq. ft.

(3.82) Cadmium-zinc (82/18) alloy, sprayed, powder pistol, 1.01 oz./sq. ft.

(5.11) Lead, electrodeposited, 0.96 oz./sq. ft.

(7.41) Tin, hot-dipped, 0.43 oz./sq. ft.†

(2.71) Cadmium, sprayed, molten-metal pistol, 0.63 oz./sq. ft.

(3.72) Cadmium-zinc (82/18) alloy, sprayed, molten-metal pistol, 0.57 oz./sq. ft.

The last two of these coatings were the most porous of those examined. The remaining eight coatings, not mentioned above, showed an intermediate degree of porosity.

It is clear that porosity is a much more serious fault in coatings of metals that are cathodic to the steel base than in coatings of anodic metals, for in the former case the corrosive attack may become concentrated on the basis metal where exposed at the pores and thus sometimes lead to pitting, whereas in the latter, the exposed steel is protected from attack by the sacrificial galvanic action of the coating. Consequently it is reassuring to find that coatings of the cathodic metals, lead, lead-tin alloy ("terne"), and tin are almost non-porous, if applied in adequate thicknesses, and it is particularly satisfactory to note that the specimen coated with the lead-tin (88/12) alloy by hot-dipping, which is fairly representative of terne plate as produced commercially, gave an excellent result in the porosity test.

(iii) *Microscopic Examination of Sections through the Coatings.*

Sections were made from a number of specimens and examined microscopically. Three photomicrographs of sections through coatings are reproduced in Figs. 17 to 19. Fig. 17 is a section through an aluminium coating sprayed by the powder pistol; the oxide inclusions usually present in sprayed coatings can be seen. Fig. 18 shows the iron-zinc alloy layer present in a hot-galvanized coating, and Fig. 19 the crystalline character of part of an electrodeposited cadmium coating; in the latter case it should be stressed that this is not typical of the smooth structure generally obtained with electrodeposited coating of thin steel sheets.

On the whole, the micro-examination indicated that the coatings were reasonably typical of normal practice for the various processes employed.

The thickness of coating on the sections prepared for microscopic examination was measured visually, using an eye-piece micrometer; about 100 individual readings were taken over a length of approximately 2 cm. It is clear that this method gives the coating thickness over the section examined only, which, owing to local variations, may not be typical of the whole surface. In most cases the minimum thickness measured on the section was about half the maximum so the thickness of sections taken from different parts of the specimen might vary to a similar degree. Clearly, the true average coating thickness could be determined only by examining a large number of sections.

It is of interest to compare the various methods of measuring coating thickness that were used in this investigation: Gain in weight after coating, magnetic thickness measurements, loss in weight on stripping, and direct microscopic determination. All four methods would be expected to yield concordant results when no interdiffusion or alloying of the coating metal with the basis steel occurs. On the other hand, when interdiffusion or alloying does occur, methods based on stripping or micro-examination would be expected to give higher values than indicated by the gain in weight after coating. The results obtained by magnetic methods of testing would depend on the magnetic properties of the diffusion or alloy layers in relation to those of the coating metal. In conformity with this, microscopic measurements made on sections through coatings in which diffusion or alloying had occurred showed, in general, an apparent coating thickness considerably greater than that calculated from the gain in weight after coating.

Considering the various methods of determining coating thickness as a whole, the results were in reasonably good agreement in certain cases, but in others discrepancies were observed.* All the evidence goes to show that the weight of the coating itself, as determined directly by weighing the specimens immediately before and immediately after its application, is by far the best criterion of average coating weight per unit area. It is desirable to supplement this by determinations of the local variations from the average thickness, and the electromagnetic thickness meter is a valuable auxiliary for this purpose.

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* For instance, in the case of zinc, microscopic examination gave a thickness value almost equal to the equivalent of the gain in weight for a coating deposited in the cyanide bath, but almost twice as great as the latter for a coating deposited in a sulphate bath. This was presumably because in the latter case the section examined was near a zone of high current density in the plating bath.

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THE DETERMINATION OF FeO IN STEEL FROM THE CARBON DROP.*

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Paper No. 38/1946 of the Ingot Committee (submitted by the Chemists' Panel of the Sub-Committee on Gaseous and Non-Metallic Inclusions).

SYNOPSIS.

The paper gives several forms of nomographs applicable to the determinations of FeO in molten steel from the carbon drop. The original basis was developed by Schenck, Riess, and Brüggemann. A variation of equilibrium temperature is included in a revised nomograph, calculated from the free-energy equations of Vacher and Hamilton. Some correlation was found with results of oxygen determinations reported by Bramley, Maddocks, and Tateson. A simpler nomograph was also constructed for use at 1600°C .

A review of the previous work on the determination of FeO in molten steel, and, on the values of the velocity and equilibrium constants required for an accurate definition of the fundamental equation governing the reaction between FeO and carbon, reveals the controversial nature of the subject and the need for further experimental enquiry to establish the accuracy of the data.

DURING the consideration of Mr. Mackenzie's paper¹ on "The Rapid Determination of Reactive Oxygen in Open-Hearth Steel" by the Liquid Steel Study Group of the Chemists' Panel of the Sub-Committee on Gaseous and Non-Metallic Inclusions, reference was made to a previous note by the present author on the application of the rate-of-carbon-drop principle to the determination of FeO in liquid steel and the use of nomographs for this purpose. As the nomographs referred to in this note had been prepared on the basis of previous data, notably that of Schenck and his co-workers,² it was agreed by the Sub-Committee that a brief review of this work would provide a useful addition to the work by Mr. Mackenzie.

A nomograph for the determination of FeO in liquid steel from a knowledge of the rate of carbon drop was referred to in the discussion of a paper by Bramley, Maddocks, and Tateson³ at a Joint Meeting of the Sheffield Society of Engineers and Metallurgists, the Sheffield Metallurgical Association, and The Iron and Steel Institute, on February 20, 1940.⁴

The suggestion of a nomograph was first made by Schenck⁵ based on the equation for $\text{FeO} + \text{C} \rightleftharpoons \text{Fe} + \text{CO}$, in the kinetic form, transposed to:

$$[\text{FeO}] = \frac{v + k'_2 p_{\text{CO}}}{k_1 [(\text{C})]},$$

where:

$v = d(\text{C})/dt$, or rate of carbon drop, percentage of carbon per minute.

$[\text{FeO}]$ and $[(\Sigma\text{C})]$ are respectively the concentrations of dissolved ferrous oxide and total carbon.

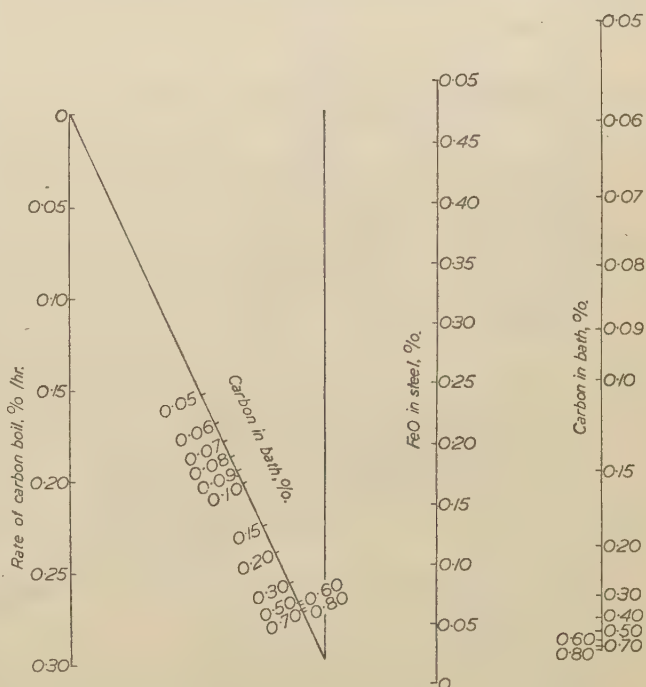


FIG. 1.—Iron Oxide Dissolved in Liquid Steel. Nomograph applicable to basic and acid open-hearth and electric furnace processes.

* Received May 20, 1946. This paper is published by the authority of the Ingot Committee. The views expressed in it are the author's, and are not necessarily endorsed by the Committee as a body.

p_{CO} is the partial pressure of the carbon monoxide at the place where the reaction occurs in the open-hearth furnace, taken as 1.1 atm.; variations are unimportant.

k_1 and k'_2 are velocity constants depending on the carbon content.

The factor k'_2 referred to here is derived from

the original equation in which this term was expressed as $k_2[FeO]p_{CO}$. As the concentration of iron, $[Fe]$, can be considered constant, this term can be written more simply as k_2p_{CO} .

In his book Schenck⁵ uses a different nomenclature in which k_2 embraces $[Fe]$ and K'_2 embraces in addition, p_{CO} .

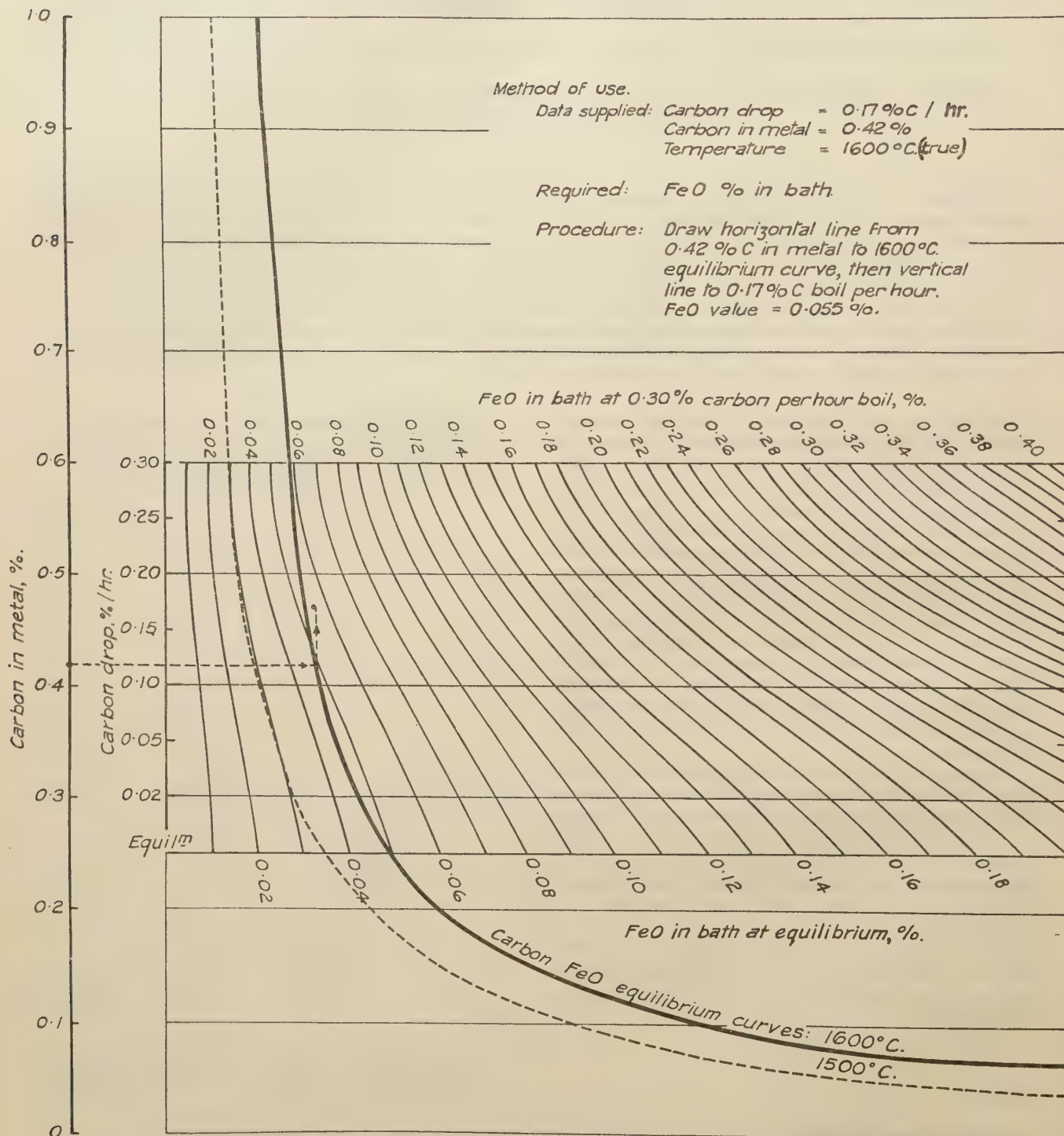


FIG. 2.—Determination of FeO in Molten Steel from carbon drop.

The equation formed the basis of a nomograph using a transparency, giving the curve of carbon drop against time for various values of FeO.

The work on which this nomograph was based is that of Schenck, Riess, and Brüggemann,² who, using a method of aluminium reduction suggested by Herty⁶, disputed his contention⁷ that the velocity constants k_1 and k_2 varied with temperature, and claimed that they varied with total carbon content.

A more convenient form of nomograph, eliminating the need for the transparency was constructed and is shown in Fig. 1.

In the discussion mentioned⁴ it was stated that a different and more convenient form of the nomograph had been devised, Fig. 2, still using the velocity constants obtained by Schenck. In this form it was possible to include the equilibrium curve, which Vacher and Hamilton⁸ claimed would vary with temperature but in a different manner from that suggested by Herty and others⁹ and in opposition to Schenck, Riess, and Brüggemann who said that temperature had no effect.

As a result of a series of experiments carried out by us under conditions approaching equilibrium, it appeared that a variation of equilibrium with temperature did occur, in the sense suggested by Vacher and Hamilton, and accordingly the temperature variation in the equilibrium curve was included in the nomograph. The variation was calculated from the free-energy equations given by Vacher and Hamilton.

Calculations using the nomograph were made with data given by Bramley, Maddocks, and Tateson in their paper, and the results as reported in the discussion⁴ showed the agreement between calculated oxygen and that obtained by vacuum fusion, to be reasonable, Fig. 3.

Later an even simpler chart was constructed for use at 1600° C. only, Fig. 4.

Although the success of the method would suggest that it is a reasonably accurate device for the purpose, the examination of the data on which the nomograph is based has shown that there has been considerable controversy over detail, and a survey of the work done in these directions may be of value.

Determinations of FeO in Steel—Survey of Work Carried Out.

Herty and others⁹ carried out extensive work on the C-FeO reaction in liquid steel in contact with slag. From this work a reasonable curve was obtained giving the variation in the equilibrium constant for this reaction. A definite variation with temperature was obtained.

The FeO was, however, determined by the Ledebur method, which was later found to be unsatisfactory in some cases, and the temperature

was determined from the MnO reaction which was not considered to be reliable above 1600° C.

Feild,¹⁰ by combining the kinetic (non-equilibrium) form of the equation $C + FeO \rightleftharpoons CO + Fe$ with the equation for diffusion of FeO across the slag-metal interface, obtained a general

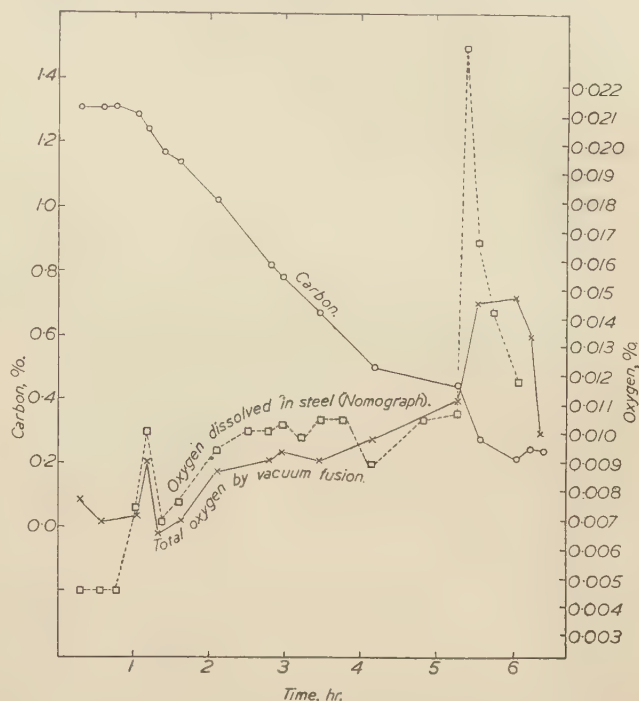


FIG. 3.—Comparison of FeO Values by Vacuum Fusion and Nomograph.

equation relating the substances in the bath. The equation in question was the following:

$$-6p \frac{dx}{dt} - \frac{m}{x_1^2} \cdot \frac{dx_1}{dt} + \frac{1}{kx_1} \left(\frac{dx_1}{dt} \right)^2 - \frac{1}{kx_1} \cdot \frac{d^2x}{dt^2} - \frac{CA}{M} \cdot w + \frac{CAm}{Mkx_1} - \frac{CA}{Mkx_1} \cdot \frac{dx_1}{dt} = 0$$

where :

x_1 = carbon in the metal, wt.-%.

p = oxidation rate, including the effect of Mn, Si, and P¹⁰ (*loc. cit.*, pp. 7-8).

m = equilibrium constant for the reaction $C + FeO \rightleftharpoons CO + Fe$.

k = kinetic or rate constant for the above reaction.

t = time, min.

C = diffusion constant, numerically equal to the rate of diffusion of FeO through the slag, in terms of lb./sq. ft. of interfacial area per min. per unit difference in concentration of FeO between the upper and lower surfaces of the slag film. It thus depends on slag composition and temperature.

A = area of bath at level of slag-metal interface, sq. ft.

M = weight of metal which comprises metal bath, lb.

w = effective FeO in the slag

(FeO + $1.35 \times \text{Fe}_2\text{O}_3$), wt.-%.

r = distribution constant (ratio of percentage concentrations of FeO in metal to FeO in slag).

Assuming that the equilibrium and kinetic constants m and k are functions of temperature, he obtained a much simpler equation relating rate of carbon drop, carbon content, FeO in metal, and temperature, as follows:

$$y = \frac{m}{x_1} - \frac{1}{kx_1} \cdot \frac{dx}{dt}$$

where y = dissolved FeO in metal, wt.-%.

The equilibrium constant he obtained from Herty,⁹ and his kinetic and diffusion constants were derived from the results of a single heat reported by Keats and Herty.¹¹ The value of 0.0306 for the equilibrium constant was expected to be too high, and to obtain real roots to his final equation he assumed a value of one third of this, i.e., 0.0102.

From his equations Feild found that the equilibrium constant depended on carbon content and temperature, and the increase in FeO when the bath was not in equilibrium was dependent upon the rate of carbon drop and not upon the carbon content.

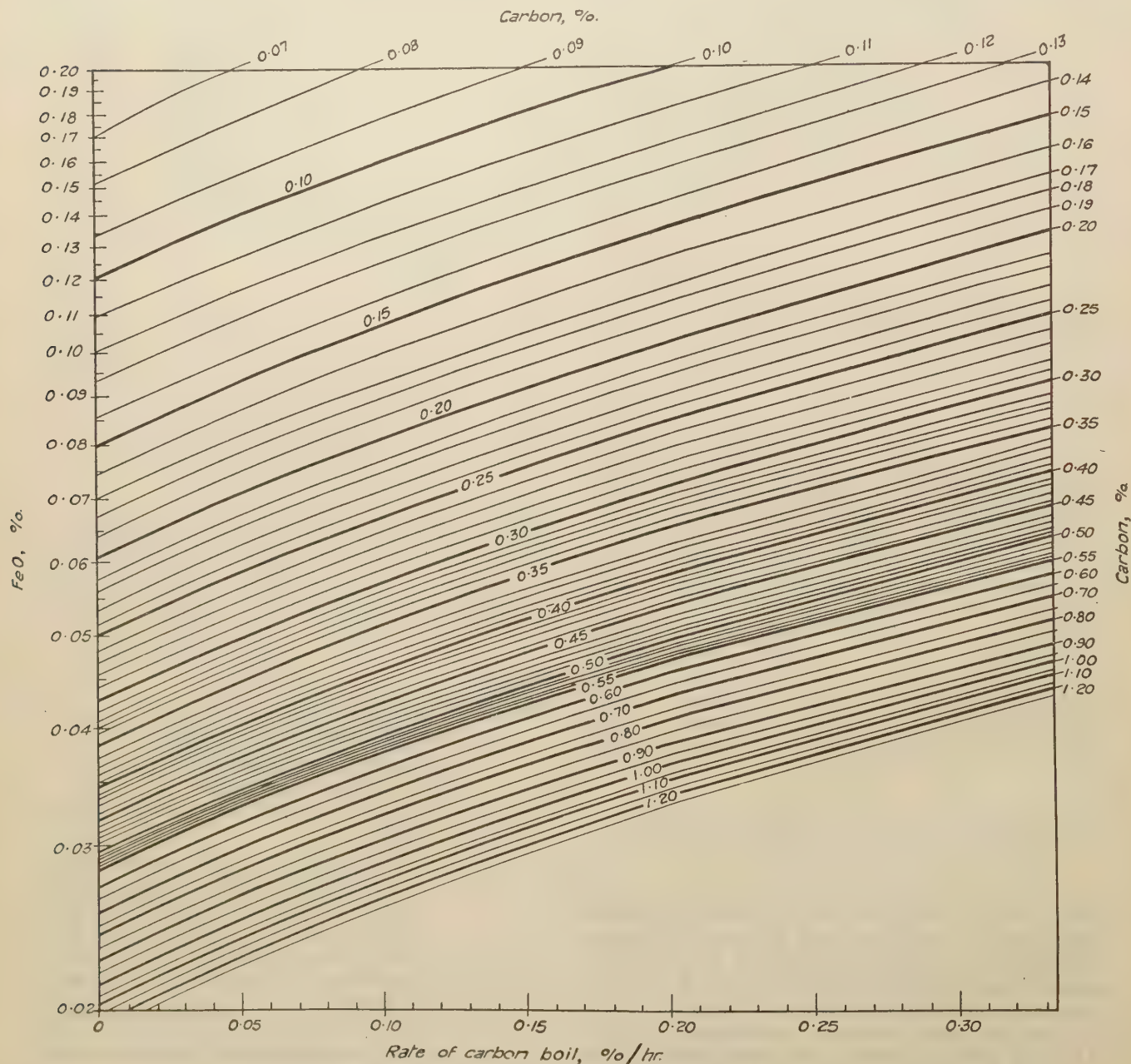


FIG. 4.—FeO-C Nomograph.

Herty¹² referred to his own previous work and estimated $K = [C] \times [FeO]$ as 0.0252 at 1600° C., but thought this value was high. One of Herty's collaborators, Larsen, in the discussion of Feild's paper estimated K as 0.016 at 1580° C. This was expected to be a better value.

Herty¹³ stated that the FeO determined by the Ledebur method was unsatisfactory owing to escape of gas on solidification of the test sample, and proposed a silicate inclusion count method to replace it.

Herty⁶ referred to the development of a method for deoxidizing FeO with aluminium, but gave no details.

Herty¹⁴ described the aluminium method for determination of FeO.

Herty⁷ referred to the use of the carbon drop for determining the FeO and indicated a general relation of velocity constants with temperature, but that other factors, *e.g.*, agitation of the bath, played a big part.

Vacher and Hamilton⁸ showed the variation in equilibrium-constant values which had been so far obtained: 0.0005 to 0.03. Many of these were calculated on uncertain premises and some were assumed values. These workers carried out certain calculations and obtained the values of two constants by taking work by Lewis and Randall¹⁵ and Garrahan,²³ which gave values at 900° C., obtained from free-energy considerations, and extrapolated these to 1600° C. The variation they obtained with temperature was again derived from calculation.

Experimental work was carried out by them and later by Vacher,¹⁷ and conclusions were derived that a value for the product of the concentrations of carbon and oxygen in the bath of 0.0023 at 1580° C. agreed with a value of 0.0025 at 1620° C. (0.0025 for $[C] \times [O]$ corresponds to 0.0112 for $[C] \times [FeO]$) and that variations due to temperature would be less than the experimental error. These figures were mean values covering rather wide variations in experimental results.

Schenck, Riess, and Brüggemann² referred to a statement by Herty¹⁸ reviewed by Schenck²⁶ and claimed that the variation in the velocity constants found by Herty could be not substantiated. Only one of his curves of $\frac{dC}{dt} / [C][FeO]$

was considered really satisfactory, namely, that at temperatures of 1570–1590° C., and as shown in Table I., taken from their paper, the variation of k_1 showed a minimum at 1600° C. which could not readily be explained and appeared unlikely.

They stated that their own results showed no effect due to temperature but claimed to observe an effect of increasing carbon content on the slope of the $\frac{d[C]}{dt} / [FeO][C]$ line. This variation is by

no means clearly marked; their lines for carbon contents of 0.0–0.20% with an average of 0.138% of carbon, and 0.21–0.40% with an average of 0.298% of carbon, are virtually the same, as shown in Fig. 5 in which the diagrams from the original paper have been superimposed. The extent of the scatter throws doubt on the validity of the conclusions.

TABLE I. *Velocity and Equilibrium Constants (after Herty).*

Temp., ° C.	k_1 .	k_2', p_{CO} .	K' .
1570–1590	0.272	0.003 ₁	80
1590–1610	0.167	0.001 ₇	100
1635	0.574	0.003 ₆	160

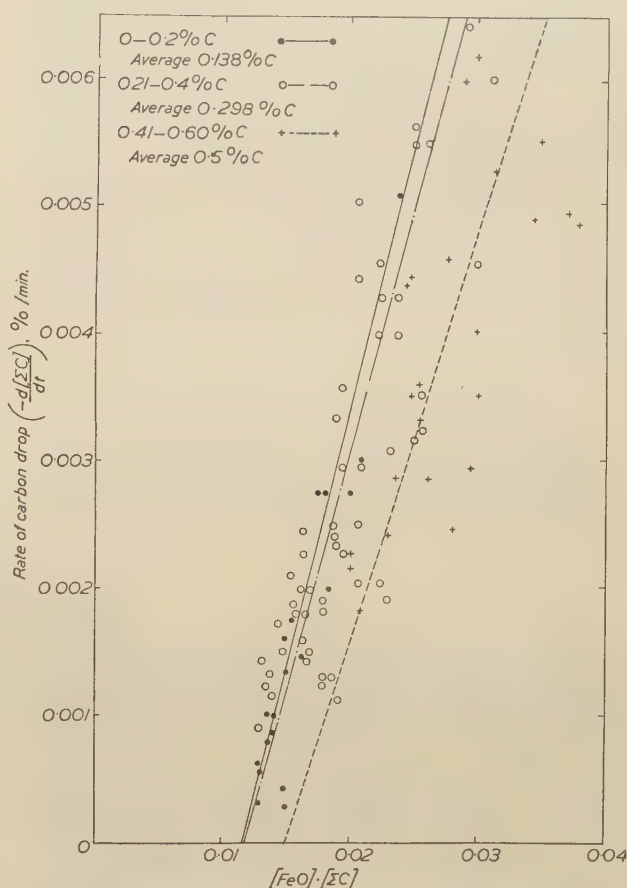


FIG. 5.—Variation of $\frac{d[C]}{dt} / [C][FeO]$ Curves with Carbon Content.

They explain this variation with carbon content as due to a polymerization of the Fe_3C , but McCance²⁰ attributes the effect to their failure to take into account the influence of gas oxidation by Fe_2O_3 in the slag and the possible variation in the activity coefficients.

McCance (*loc. cit.*) states that no systematic investigation of the $[\text{FeO}] \times [\text{C}]$ constant at various temperatures has so far been carried out. Using the heat of reaction of the equation, $\text{FeO} + \text{C} = \text{CO} + \text{Fe}$, at $1500\text{--}1600^\circ \text{C.}$, which he estimates at 28.5 cal. , and the value of the constant obtained by Vacher and Hamilton⁸ at 1620°C. of 0.011, he expresses the temperature relationship of the constant as:

$$\log K = -\frac{6230}{\text{Temp.}(^\circ\text{K.})} + 5.246.$$

The first attempt at a nomograph for determining FeO from the rate of carbon drop was made by Schenck.² As stated above this has been modified as shown in Figs. 1, 2, and 4.

It is apparent from the controversial nature of the above that the basis upon which such types of nomographs can be constructed is inadequate. The temperature of the bath can now be measured directly by means of the quick-immersion pyrometer, and much progress has been made in the determination of oxygen in liquid steel. A much sounder basis, therefore, now exists for the obtaining of experimental data necessary to improve the accuracy of such nomographs.

The author is indebted to Dr. R. Jackson for his valuable assistance in making a critical re-examination of the literature for the purpose of this note.

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CORRESPONDENCE.

MR. N. F. DUFTY (K. and L. Steelfounders and Engineers, Ltd., Letchworth) wrote: In the first place the writer considers the foundations on which this method of determining FeO in liquid steel are based to be entirely fallacious. It is rather sweeping to make the assumption that appreciable concentrations of reactants in excess of equilibrium values can exist in a monophasic liquid at $1600^\circ \pm 40^\circ \text{C.}$

Styri asserts that equilibrium is reached between $[\text{C}]$ and $[\text{FeO}]$, explaining the excess of $[\text{FeO}]$ on the grounds that some of it is bound up in compounds having low dissociation pressures, for instance, silicates and aluminates. Unfortunately for this theory there is little concrete evidence to support it.

Apart from this, two other theories can be considered. The FeO-carbon reaction may occur, but in the absence of bubbles a back pressure

of CO may build up. Physical conditions governing bubble formation would then decide the reaction rate, not concentrations or activities. This theory would entail some explanation of why the back pressure of CO was higher on high-carbon steels, which it must be with a constant excess $[\text{FeO}]$. As this explanation is not forthcoming this theory must be discarded. Alternatively the reaction may be non-homogeneous and occur at the gas-metal interface, its velocity depending on the gas-metal contact area, *i.e.*, bubble formation, and the rate of reactant supply to the zone of reaction.

The slowness of the carbon reaction may be attributed to the slow speed of diffusion of FeO from the slag. This cannot be so because of the amount of $[\text{FeO}]$ in excess of the equilibrium figure, indicating that there is normally adequate transfer from the slag. In view of the oxygen

pressure differential between the furnace atmosphere and the metal, this is not surprising. Again one is forced to the conclusion that bubble formation is the controlling factor. There are many instances to support this contention.

Korber and Oelsen, when investigating equilibria in silica crucibles under iron-manganese-silicate slags, found that boiling did not occur until the $[C][FeO]$ product was ten to fifteen times the equilibrium value. However, boiling started as soon as the crucible wall was scratched or an iron wire introduced. As the crucible became more glazed the reaction became more difficult to initiate.

The writer has experienced many such examples in both acid open-hearth and basic-electric furnaces. The silicon reduction phenomenon may occur early in the acid open-hearth heat, even when the slag contains 40% of FeO, because temperature is the governing factor and the silica of the hearth is reduced, not that of the slag. In such cases the bath goes off the boil as the $[FeO]$ content in the area immediately adjacent to the hearth is reduced by the silicon increment and the boil cannot be initiated at its usual site, the hearth-metal interface. In the upper layers of the bath the $[FeO]$ value remains well in excess of its equilibrium value with the bath carbon and yet there is no boiling action. If the temperature is lowered to a point at which silicon is no longer reduced from the hearth, boiling resumes with added violence.

In the electric furnace, owing to an unfavourable charge or unusual melting conditions, a portion of the scrap may melt, run down onto the hearth, and set there. It is extremely difficult to start a boil under these conditions and a considerable

excess of $[FeO]$ must be present before a boil will commence. Once started, the reaction becomes autocatalytic and an exceptionally vigorous boil results.

Why a rough surface should favour bubble formation is not known with any degree of exactitude. It may well be that there are tiny crevices which the liquid steel cannot fill owing to its surface tension. Gas can diffuse into these voids, forming bubbles which rise up through the bath. Brower and Larsen state that a statistical analysis of a large number of heats indicates that the rate of carbon elimination may vary fivefold for a given excess $[FeO]$ above the equilibrium value. They also give evidence that conditions governing bubble formation do have an appreciable effect on this excess $[FeO]$. The measured excess $[FeO]$ was found to be repeatedly lower on heats made in furnaces with clean hearths than on those made in furnaces with hearths contaminated and glazed by slag and lime from previous heats, particularly high-carbon heats.

Another important point was brought out by the fact that boils induced by limestone or completely non-oxidizing agencies, such as stirring rods, green poles, cold blooms, &c., brought about a temporary reduction in the excess $[FeO]$ because, by initiating bubble formation, conditions favourable for the attainment of equilibrium between carbon and $[FeO]$ were created. In all cases the excess $[FeO]$ resumed its former level once the artificially stimulated boil had subsided.

In conclusion it is hoped that this paper and the discussion stimulated by it will result in further work on the equilibrium between carbon and FeO in solution in liquid iron, particularly work of a practical nature.

AUTHOR'S REPLY.

The AUTHOR wrote in reply: It is noted with interest that Mr. Dufty agrees with the main conclusion of the paper, *viz.*, that further experimental inquiry is required to establish more accurately the relation between the rate of carbon drop and the FeO in the steel. One might go further and, to replace the term FeO, use the term "oxygen in all its combinations which may have a bearing upon the properties of the steel." In spite of the difficulties in establishing the existence of an FeO-carbon reaction as a useful criterion in steelmaking practice, the carbon drop is a critical feature of the changes in the oxidation process. It is readily observed, and accordingly offers a promising line of investigation. The difficulties relating to bubble formation may at times produce obstacles which would invalidate the applicability of any relationship worked out, either from theoretical considerations or from experimental investigation. In general, however,

the problems encountered apply to the normal condition of the bath, and even bubble formation must follow certain natural laws. Such a factor should be capable of being taken care of in the establishment of the relations discussed in the paper.

To use the term "entirely fallacious" as an assessment of the value of the work that has already been done is, in the author's opinion, over-sweeping. The exponents of the efforts which have been made towards the establishment of a carbon-FeO relation might be entitled to consider that, where measured values were concerned, criticism which had little quantitative basis was equally invalid. Nevertheless, Mr. Dufty's comments are to be welcomed, as indicating important practical obstacles which must be considered in any further approach to the problems discussed.

THE FORMULATION OF ANTI-CORROSIVE COMPOSITIONS FOR SHIPS' BOTTOMS AND UNDER-WATER SERVICE ON STEEL.—PART II.*

By F. FANCUTT, F.R.I.C., A.M.I.CHEM.E. (DERBY), AND J. C. HUDSON, D.Sc. (BIRMINGHAM;
OFFICIAL INVESTIGATOR TO THE CORROSION COMMITTEE).

(Figs. 7 and 8 = Plates XLI. and XLII.)

Paper No. 18/1946 of the Corrosion Committee (submitted by the Marine Corrosion Sub-Committee).

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SYNOPSIS.

A second series of raft tests by the Marine Corrosion Sub-Committee on anti-corrosive paints for underwater use on ships' bottoms has confirmed the earlier results and enlarged them considerably. One hundred and twenty-seven new formulated anti-corrosive paints were made for the purpose and comprised various combinations of 8 different media with mixtures of 13 different pigments. On the basis of the results, paint No. 173, pigmented with a mixture of 2 parts of basic lead sulphate and 1 part each of white lead, Burntisland red, and barytes, and bound in a modified phenol-formaldehyde/litho-oil medium

* Received January 28, 1946. This paper is published by authority of the Corrosion Committee. The views expressed in it are the authors', and are not necessarily endorsed by the Committee as a body.

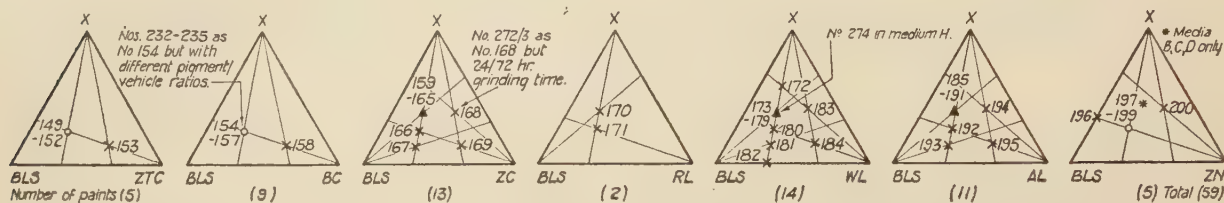
is suggested for general use at this stage. Several other paints gave an even better performance in the raft tests than paint No. 173 and merit further investigation. Paints in a chlorinated-rubber medium were outstanding but certain technical difficulties need to be overcome before these can be used effectively on a practical scale.

INTRODUCTION.

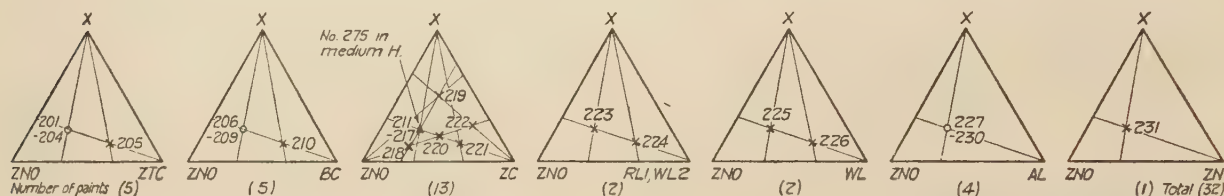
IN an earlier publication * the authors presented the results of two series of raft tests conducted at Caernarvon and Emsworth, respectively, which constituted the first stages in the systematic study of anti-corrosive paints for ships' bottoms that is being conducted by the Marine Corrosion

formulations based on basic lead sulphate were found to be of particular promise, especially when aluminium or white lead was incorporated in the pigment mixture; as regards the medium, various types of phenolic- or coumarone-resin varnish and a medium containing chlorinated rubber proved to be the best of the range of vehicles tested.

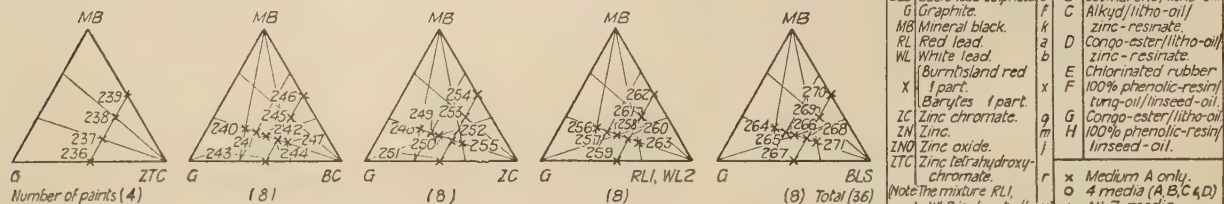
BASIC LEAD SULPHATE SERIES



ZINC OXIDE SERIES



GRAPHITE AND MINERAL BLACK SERIES



Pigments.		Media.	
AL	Aluminium.	g	A Modified-phenol-formaldehyde/litho-oil
BC	Barium chromate	n	B Coumarone/litho-oil
BLS	Basic lead sulphate	c	C Alkyd/litho-oil
G	Graphite.	f	D Congo-ester/litho-oil
MB	Mineral black.	k	E 100% phenolic-resin/tung-oil/linseed-oil
RL	Red lead.	a	F Chlorinated rubber
WL	White lead.	b	G 100% phenolic-resin/linseed-oil
X	Burnt/Island red	x	H 100% phenolic-resin/linseed-oil
Y	Barites 1 part.		
ZC	Zinc chromate.	g	
ZN	Zinc.	m	
ZNO	Zinc oxide.	j	
ZTC	Zinc tetrahydroxy-chromate.	r	

FIG. 1.—Formulation of Anti-Corrosive Paints Nos. 149-275.

Sub-Committee. These tests were intended to serve as a preliminary survey of the effects of pigmentation and of binder on the performance of paints used for the protection of steel immersed in sea-water. Thus, with a few exceptions, the paints tested in the Caernarvon series were all bound in the same medium, a modified phenol-formaldehyde/stand-oil varnish, differences in the pigment mixtures being the main variable, whilst at Emsworth the number of pigment mixtures was restricted to three but each was incorporated in 21 different media.

The results of this work may be summarized by the statement that, as regards pigmentation,

The next stage in the investigation was the study of the effects of combining the best pigment combinations with the most promising media. This the authors have endeavoured to do, and the present paper deals with the results of immersion tests in sea-water conducted on a further 127 formulated anti-corrosive paints applied to steel plates in a weathered condition. As in previous work, two coats of each anti-corrosive paint were applied to the specimens; the painting was completed by applying a finishing coat of a formulated anti-fouling composition, reference AF10/43, which was the same throughout. The tests were conducted at Caernarvon from November 1943 to

* F. Fancutt and J. C. Hudson, *Journal of The Iron and Steel Institute*, 1944, No. II., p. 269 p.

July 1944 and extended over a period of 40 weeks.

A.—EXPERIMENTAL.

(1) General Scheme of the Tests.

(a) Formulation of the Paints Tested.

The 127 anti-corrosive paints included in the present investigation carry the serial numbers 149 to 275. Their formulations are shown diagrammatically in Fig. 1, where the composition of each pigment mixture tested is represented by means of triangular co-ordinates.* In order to facilitate comparison, these compositions were selected to correspond with the points of intersection of the lines joining the apices of the equilateral triangle to the points of trisection of the opposite side, either with each other or with

position, reference AF10/43, was prepared and used as a finishing coat over all the protective-painting schemes. Details of the composition are as follows :

Cuprous oxide	16 wt.-%.
Mercuric oxide	8 "
Burntisland red	14 "
Zinc oxide	2 "
Asbestine	6 "
Rosin	21 "
Modified phenol-formaldehyde/ stand-oil varnish †	11 "
Pine oil	2 "
Naphtha	20 "

Specific gravity of paint at 70° F.	1.50
Efflux time ‡	80 sec.
Total volatile content	24.3%
Specific gravity of total volatile matter	0.854

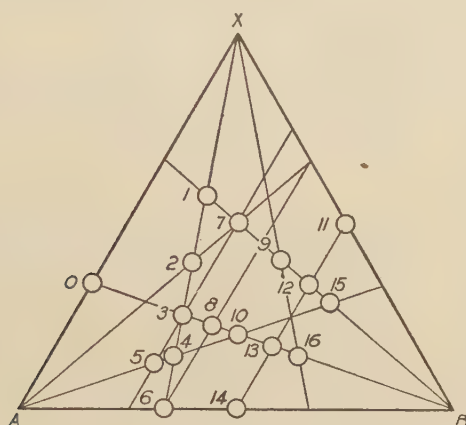


FIG. 2.—Pigment Ratios by Weight.

Point No.	Ratios.			Percentage.		
	A	B	X	A	B	X
0	2	0	1	67	0	33
1	2	1	4	29	14	57
2	2	1	2	40	20	40
3	2	1	1	50	25	25
4	4	2	1	57	29	14
5	5	2	1	63	25	12
6	2	1	0	67	33	0
7	1	1	2	25	25	50
8	4	3	2	45	33	22
9	1	2	2	20	40	40
10	2	2	1	40	40	20
11	0	1	1	0	50	50
12	1	3	2	17	50	33
13	2	3	1	33	50	17
14	1	1	0	50	50	0
15	1	4	2	14	57	29
16	2	4	1	29	57	14

lines parallel to one of the sides. As a result the various constituents are present in simple proportions by weight as shown in Fig. 2.

The paints are classified in three groups :

(i) *Basic lead sulphate series*.—A group of 59 paints, Nos. 149–200, 232–235, and 272–274, pigmented with mixtures based on basic lead sulphate.

(ii) *Zinc oxide series*.—A group of 32 paints, Nos. 201–231 and No. 275, pigmented with mixtures based on zinc oxide.

(iii) *Graphite and mineral black series*.—A group of 36 paints, Nos. 236–271, pigmented with ternary mixtures of graphite, mineral black, and an inhibitive pigment.

In addition, a formulated anti-fouling com-

The composition was manufactured by dissolving the resin in 17 parts of naphtha, adding the toxins, and ball-milling for 2 hr. The remaining ingredients were then mixed and added to the mill, after which milling was continued for a further 15 hr.

(b) Basic Lead Sulphate Series and Zinc Oxide Series.

The paints included in the basic lead sulphate series and the zinc oxide series constitute the larger part of the experimental programme. Throughout these two groups the composition of the pigment mixture was varied so as to study the effect of additions to basic lead sulphate or zinc oxide, respectively, of varying proportions of

* In this connection the authors have pleasure in acknowledging their indebtedness to E. W. McMullen and E. J. Ritchie, whose paper, "Organisation of a Systematic Test Fence Programme" (*Industrial and Engineering Chemistry*, 1943, vol. 35, p. 161) proved a profitable source of study when the work was being planned.

† Medium No. 2 of the earlier investigation (*loc. cit.*, p. 318 P); it consists of modified phenol-formaldehyde resin (Bedesol 66), 64 parts; medium stand-oil, 128 parts; white spirit, 124 parts; and lead-cobalt-manganese drier, 3½ parts.

Its method of manufacture is: Heat stand-oil to 220° C.; add resin and heat to 240° C. until clear (approx. ½ hr.); cool to 180° C. and add thinner and driers.

‡ Efflux time for the first 50 c.c. from a full No. 4 Ford cup, at 70° F.

seven inhibitive pigments: Zinc tetrahydroxy-chromate, barium chromate, zinc chromate, red lead,* white lead, aluminium, and zinc; in the majority of cases a diluting pigment was also added. For the sake of simplicity the same extender has been used throughout, namely, a mixture of equal parts by weight of Burntisland red and barytes.

The following eight paint media were used:

- A Modified phenol-formaldehyde/litho-oil.
- B Coumarone/litho-oil.
- C Alkyd/litho-oil/zinc-resinate
- D Congo-ester/litho-oil/zinc-resinate
- E Chlorinated rubber
- F 100% phenolic-resin/tung-oil/linseed-oil
- G Congo-ester/litho-oil
- H 100% phenolic-resin/linseed-oil.

Details of the formulation of these media will be found in Appendix A, but the composition of medium A (modified phenol-formaldehyde/litho-oil), the most widely used of all, may be noted here:

Modified phenol-formaldehyde resin (Bedesol 66), %	21.25
Heavy litho-oil, %	42.50
Naphtha, %	35.40
Lead naphthenate (Pb 24%), %	0.68
Cobalt naphthenate (Co 6%), %	0.17

A complete set of paints incorporating each of the pigment combinations shown in Fig. 1 was made in this medium, but only selected pigment mixtures were incorporated in the other seven media. The following four pigmentations were common to media A to G:

		Parts by weight,
(i) <i>cqx</i> 212	Basic lead sulphate . . .	2
	Zinc chromate . . .	1
	Extender . . .	2
(ii) <i>cbx</i> 212	Basic lead sulphate . . .	2
	White lead . . .	1
	Extender . . .	2
(iii) <i>cgx</i> 212	Basic lead sulphate . . .	2
	Aluminium . . .	1
	Extender . . .	2
(iv) <i>jgx</i> 211	Zinc oxide . . .	2
	Zinc chromate . . .	1
	Extender . . .	1

A few additional paints were made as follows:

(i) Four paints (Nos. 232-235) were made similarly to paint No. 154 (*cnx* 211/A)†; the same pigmentation and medium were used, but with different pigment/vehicle ratios. These five paints constitute a series in which the pigment/vehicle ratio varies in steps from 2.7 to 7.9.

(ii) In order to study the possible effect of differences in milling time, two paints, Nos. 272

and 273, were prepared, each differing from paint No. 168 (*cqx* 122/A) only in that they were ground in a ball mill for 24 and 72 hr., respectively, as compared with a period of 12 hr. for paint No. 168.

(c) Graphite and Mineral Black Series.

The main object in making the 36 paints of this group was to develop improved black or dark brown anti-corrosive paints for certain naval purposes. The tests were planned in such a way as to yield a comparison of the merits of five different inhibitive pigments, zinc tetrahydroxy-chromate, barium chromate, zinc chromate, a mixture of 1 part of red lead with 2 parts of white lead, and basic lead sulphate, when incorporated with various combinations of graphite and mineral black. The percentage of inhibitive pigment present in the mixture varied from 25 to 57 by weight.

The only medium used throughout this series of paints was medium A (modified phenol-formaldehyde/litho-oil).

(2) Preparation of the Paints.

In general, the pigment/non-volatile-vehicle ratios in the paints were selected in relation to the oil-absorption values of the pigments, as determined experimentally.

The paints were prepared in $\frac{1}{2}$ -gal. lots by mixing the requisite proportions of pigments and medium, thinning to a suitable consistency with naphtha, and ball-milling for 12 hr.‡ The milled paints were then allowed to stand at 70° F. for 1 week, after which a brushing-out test was made and the consistency finally adjusted, where necessary, by the addition of naphtha. The efflux time (Ford cup) and the specific gravity of each paint were then determined. In each case, as far as was practicable, the consistency of the paint was adjusted to give an efflux time of 40 ± 5 sec. for the first 50 c.c. from a full No. 4 Ford cup at 70° F. for paints of the basic lead sulphate group and approximately 60 sec. and 80 sec., respectively, for paints of the zinc oxide and of the graphite and mineral black groups.

In the case of paints containing aluminium, this pigment was first mixed with part of the appropriate medium and added in the requisite quantity to the remainder of the paint prepared by the normal ball-milling. Zinc dust, when incorporated, was mixed into the prepared paint after milling.

All the pigments used were taken from the same

* In the case of the zinc oxide group of paints it was considered preferable to substitute a mixture of 2 parts of white lead with 1 part of red lead (by weight) for red lead alone.

† The code method of designating paint formulations is as follows: The minuscule letters denote the pigments and the figures denote their respective proportions by weight; the medium is indicated by the capital letter following the stroke. Hence paint No. 154 consists of 2 parts of basic lead sulphate, 1 part of barium chromate, and 1 part of mixed extender in medium A (modified phenol-formaldehyde/litho-oil).

‡ A special procedure was adopted in the case of paints in the chlorinated-rubber medium E (see Appendix A).

TABLE I.—Composition of the Pigments.

Pigment.	Complies with B.S.S. No.—	Additional Information.
<i>a</i> Red lead, non-setting	217/1936 (Type C)	97.0% Pb_3O_4 .
<i>b</i> White lead	239/1935	77.2% PbCO_3 , 22.6% Pb(OH)_2 .
<i>c</i> Basic lead sulphate	637/1935	74.7% PbSO_4 , 22.1% PbO , 1.2% ZnO .
<i>d</i> Burntisland red *	...	46.0% Fe_2O_3 .
<i>e</i> Barytes (Hopton)	...	66.3% BaSO_4 .
<i>f</i> Graphite	...	36.2% Graphitic carbon.
<i>g</i> Aluminium powder	388/1938	Passes 200 I.M.M. standard screen.
<i>j</i> Zinc oxide	254/1935 (Type I., Grade L)	99.2% ZnO .
<i>k</i> Mineral black	288/1937	59.8% Ash on ignition.
<i>m</i> Zinc dust	...	97.2% Zn , 1.9% ZnO .
<i>n</i> Barium chromate	...	35.9% CrO_3 , 57.2% BaO .
<i>q</i> Zinc chromate	389/1938	37.0% CrO_3 , 43.0% ZnO .
<i>r</i> Zinc tetrahydroxy-chromate	...	18.2% CrO_3 , 68.5% ZnO .†
<i>x</i> Extender	...	A mixture of equal parts by weight of <i>d</i> Burntisland red and <i>e</i> extender.

* Burntisland red is the washed and calcined residue left after the recovery of aluminium from bauxite.

† Approximates to $\text{ZnCrO}_4 \cdot 4\text{Zn(OH)}_2$.

batch in each case; particulars of their composition are given in Table I. With the exception of the two 100% phenolic-resin media (*F* and *H*), the media were prepared under supervision in an industrial plant to the formulations given in Appendix A.

(3) Storage Tests.

Separate samples of each paint, contained in 1-pint tins fitted with $1\frac{1}{2}$ -in. Farwig caps, were subjected to storage tests for periods of approximately 6 months under two conditions: (i) At ordinary room temperature, and (ii) at a constant temperature of 120° F.; the latter test was carried out in a climatic hut through the kindness of the Chief Superintendent, Armament Research Department.

(4) Surface Preparation of the Specimens.

Steel specimens $15 \times 10 \times \frac{1}{4}$ in. were used for the tests; they were cut from two batches of $\frac{1}{4}$ -in. plate of the following analyses:

C, %.	Mn, %.	Si, %.	P, %.	S, %.	Cu, %.
(i) Acid open-hearth steel.					
0.17	0.53	0.03	0.05	0.05	0.15
(ii) Basic open-hearth steel.					
0.17	0.67	0.10	0.02	0.04	...

The specimens on which the paints of the basic lead sulphate series and of the zinc oxide series were tested were all taken from batch (i).

Each painting scheme, consisting of 2 coats of formulated anti-corrosive paint and 1 coat of anti-fouling composition AF10/43, was tested on duplicate specimens that had been weathered outdoors at Birmingham for 6 months in the case of the basic lead sulphate and the zinc oxide

series, and for 2 months in that of the graphite and mineral black series.† One specimen of each pair was exposed to the weather in the as-rolled condition, and the other was pickled in cold hydrochloric acid (5% by volume) before exposure.

At the conclusion of the weathering period all the specimens were cleaned by means of a portable electrical wire-wheel brush. This was applied for approximately 45 sec. to each face; the edges were wire-brushed by hand for a further 30 sec. This corresponded approximately to a cleaning rate of 60 sq. ft./hr. A final light brushing with a hand wire-brush was given immediately before painting.

The loss in weight on weathering of all specimens was determined and the percentage descaling of each as-rolled surface was estimated. These observations are summarized in Table II.

(5) Painting of the Specimens.

The specimens were painted under cover at Caernarvon. The first coats of all the paints were applied in succession during the period November 10–14, 1943; the order of painting was determined by lot. Thereafter the specimens were dealt with in batches of 40 or 48, which is the maximum number that it was possible to immerse on one day. The preparation and exposure of each batch was completed before proceeding with the next. The second coats were applied to all the specimens of a given batch on the same day and on the following morning the final coat of anti-fouling composition AF10/43 was applied; thus the drying time allowed for the second anti-corrosive coat varied from about 18 to 24 hr. The specimens were immersed from the raft

† In the case of paints Nos. 274 and 275, owing to shortage of materials, specimens prepared by shot-blasting were substituted for the as-rolled and weathered specimens. The second specimen of each pair was prepared in the normal manner, by pickling followed by weathering for 2 months.

TABLE II.—*Loss in Weight and Descaling of the Specimens after the Preliminary Weathering.*

Number of Specimens.	Used for Paints Nos.—	Specimen.*	Property.†	Min.	Max.	Mean, \bar{x} .	Standard Deviation, σ .	90% Range.‡
87 §	149-235	I.	Loss in weight, g. Descaling, %.	13.5 7	30 86	19.4 35.4	4.0 18.9	14-28 12-71
		II.	Loss in weight, g.	-4	3	-1.3	1.5	(-3)-1
40	236-275	I.	Loss in weight, g. Descaling, %.	6.5 3	15 24	10.6 10.1	2.1 5.5	7-14 4-20
		II.	Loss in weight, g.	-2	2	-0.2	1.2	(-2)- 1.5

* I. Exposed to weathering in the as-rolled condition. II. Mill scale removed by pickling before exposure to weathering.

† *Loss in Weight, g.*—This was determined after cleaning with wire-brushes, as described in the text.

Descaling, %.—These determinations were made through a grid as described in section A, sub-section (8), and refer to the central 100 sq. in. of the specimen. Descaling at the edges had penetrated inwards in certain cases up to a maximum distance of 1.5-2 in.

‡ For a symmetrical normal distribution, this range, which includes 90% of the individual observations, is $\bar{x} \pm 1.645 \sigma$. The distributions under consideration were asymmetrical and the ranges given have been determined by inspection.

§ All specimens of steel (i) weathered for 6 months (April-October, 1943).

|| Twelve specimens of steel (i) and 28 of steel (ii), weathered for 2 months (August-October, 1943). In case I. only, the data refer to 38 specimens, because the specimens of this set coated with paints Nos. 274 and 275 were prepared by shot-blasting and were not weathered.

TABLE III.—*Details of Painting the Specimens.*

		Max.	Min.	Mean.	Standard Deviation.	90% Range.¶
Atmospheric temperature, ° F. (84 observations) .		55	32.5	44	5	36-52
Relative humidity, % (84 observations)		100	74	93	7	81-100
Spreading Rates of Paints, sq. yd./gal.**						
<i>Basic Lead Sulphate and Zinc Oxide Groups (87 Paints).</i>						
1st coat AC 1	I.	98.2	46.5	66.9	11.4	48.1-85.7
	II.	92.3	43.0	67.6	10.0	51.1-84.1
2nd coat AC 2	I.	106.8	41.5	61.1	12.0	41.4-80.8
	II.	90.2	43.0	60.8	9.6	45.0-76.6
3rd coat AF 3	I.	74.6	42.6	55.2	6.3	44.8-65.6
	II.	69.8	43.2	55.3	4.7	47.6-63.0
<i>Graphite and Mineral Black Group (36 Paints).</i>						
1st coat AC 1	I.	88.8	49.2	67.2	10.9	49.3-85.1
	II.	82.3	43.4	61.3	8.5	47.3-75.3
2nd coat AC 2	I.	69.3	44.3	55.4	7.6	42.9-67.9
	II.	72.8	41.8	57.0	7.4	44.8-69.2
3rd coat AF 3	I.	69.8	43.2	53.9	5.0	45.7-62.1
	II.	65.6	37.3	54.6	5.2	46.0-63.2

¶ Approximate limiting values containing 90% of the observations calculated as the mean value ± 1.645 times the standard deviation.

** I. As-rolled and weathered specimens.

II. Pickled and weathered specimens.

during the afternoon of the day on which they had received the anti-fouling coat, after a drying interval of not less than 4 hr.; the maximum figure recorded for this interval was $6\frac{1}{2}$ hr.

The weight of wet paint used was determined for all three coats by weighing the paint container, &c., before and after coating each specimen. The weight of dry paint on each specimen was also determined directly in the case of the anti-

corrosive coats only. The rate of application aimed at in formulating the paints was approximately 60 sq. yd./gal. for each coat; this spreading rate was deliberately made lower than in the previous tests so as to reduce the disparity in this respect between these small specimens and actual ships. Data concerning the painting of the specimens are given in Table III. and further details will be found in Appendix B.

(6) *Conditions of Immersion at Caernarvon.*

The specimens were exposed on the larger raft at Caernarvon.* Duplicate specimens were placed in opposite halves of the raft but, subject to this and the exigencies of the painting-programme, their positions were chosen at random. The specimens of the basic lead sulphate and the zinc oxide series were arranged on double frames, *i.e.*, frames carrying two rows of vertical specimens immersed at depths (measured to the top edges) of 18–24 in. and 36–42 in., respectively; one specimen of each pair was immersed at each depth. The specimens of the graphite and mineral black series were exposed on single frames at the shallower of the two depths. Immersion of the specimens took place at various dates from November 16 to 26, 1943.

(7) *Inspections during Exposure.*

Six inspections of the specimens were made at the raft during the period between their immersion in November, 1943, and their removal on August 29–31, 1944, after an average period of exposure of 40 weeks. At each inspection systematic records of the fouling and of the condition of the paint film on each test surface were taken in the standard manner as described previously.†

(8) *Final Examination in the Laboratory.*

Immediately after removal from the water at the end of the test, the specimens were freed from fouling by means of scrapers and fibre brooms. A further cleaning with fresh water and fibre brooms was given after the specimens had been taken ashore. On return to the laboratory each surface was examined. To facilitate this, a grid was superposed on the specimen, which masked the edges and subdivided the remaining central area of 100 sq. in. into six equal areas of approximately 16 sq. in. each. Separate estimates of the following quantities were made for each of the six sub-areas on each face, the individual figures being aggregated or averaged, as expedient, so as to yield a representative value for the whole specimen: ‡

- Item A Complete paint film intact, *i.e.*, anti-fouling coat still adherent, percentage by area.
- Item B Anti-corrosive paint only intact (one or both coats), percentage by area.
- Item C Bare but unruined steel, percentage by area.

- Item D Rusted metal, percentage by area.
- Item E Depth of any pits, mils.§

In addition, the specimens were reweighed after the final cleaning, the differences between these weighings and the corresponding weights of the fully painted specimens being taken as the losses in weight.

B.—RESULTS.

(1) *Fouling.*

The new formulated anti-fouling composition AF10/43 proved to be much better than its predecessors, AF8/42 and AF1/43, used in the previous tests at Caernarvon and Emsworth, respectively. No serious fouling occurred on the specimens throughout the winter months, but in the spring of 1944 the surfaces began to foul. During the months of April and May weed was observed on specimens in the upper row and some barnacles settled on those in the lower row. A certain positional effect as regards fouling was observed, but it is improbable that this had any marked influence on the protective properties of the paint films. This difference in fouling was due in part to the accumulation of drifting weed in some of the end bays as a result of the fair-weather being carried away in an abnormally severe storm, and in part to the growth of long laminaria on the timbers and drums, which scoured some of the specimens in the immediate vicinity.

The fouling organisms on the specimens did not grow rapidly, but towards the end of the exposure period they interfered somewhat with observations of the specimens and this factor was largely responsible for the discontinuation of the tests after 40 weeks. In other words, the life of the anti-fouling composition proved to be less than that of the best anti-corrosive coatings beneath it.

(2) *Comparison of the Anti-Corrosive Paints.*

Any comparison of the relative merits of the anti-corrosive paints included in this investigation necessarily involves the assessment of a number of different factors and it is difficult to attach the correct weight to each. It is desirable, therefore, to compound the various factors so as to provide as simple an index as possible of the behaviours of the paints when making the final assessment. Accordingly, as in the earlier series of tests, the

* Details of the Caernarvon raft and the method of exposure will be found in the First Report of the Marine Corrosion Sub-Committee, *Journal of The Iron and Steel Institute*, 1943, No. I., p. 355 P.

† First Report of the Marine Corrosion Sub-Committee, *loc. cit.*, p. 356 P.

‡ It will be seen that this procedure eliminates the effects of any breakdown at the edges.

§ The pits were also classified thus :
f fine, less than 2 mm. dia.
m medium, 2–10 mm. dia.
c coarse, more than 10 mm. dia.

TABLE IV.—*Classification of the Results.*

Grade.	Mark.	Lower Limit of Grade, percentage of array from top.	Positions in Order of Merit included in Grade.*	
			Basic Lead Sulphate and Zinc Oxide Series (87 paints).	Graphite and Mineral Black Series (36 paints).
Very good	3	12.31	Nos. 1-11	Nos. 1- 4
Good	2	30.77	Nos. 12-27	Nos. 5-11
Moderate	1	58.46	Nos. 28-51	Nos. 12-21
Bad	0	100.00	Nos. 52-87	Nos. 22-36

* In the case of a tie for the last place or places in a given grade, all the paints concerned have been included in that grade.

authors have again decided to deduce a single merit figure based on the following observations :

(i) The total "index figure" deduced from the visual inspections made throughout the exposure. This is calculated by adding together the 12 returns for the percentage blistering (one figure for the front surface and one figure for the back surface at each of the six inspections), twice the sum of the 12 returns for the percentage flaking, and ten times the sum of the 12 returns for the percentage rusting.†

(ii) The "index figure" for rusting alone, calculated as in (i).

(iii) The area over which the complete paint film was found to be intact at the final laboratory examination.‡

(iv) The amount of rusting, as determined at the final laboratory examination.§

(v) The loss in weight, determined as in section A, sub-section (8).

In each case results are available for duplicate specimens, so that for any one paint 10 different figures have to be taken into consideration.

The merit figure has been deduced as follows : The paints have been arranged in decreasing order of merit according to each of the 10 sets of observations, the 87 paints || of the basic lead sulphate and the zinc oxide series being considered separately from the 36 paints of the graphite and mineral black series. In each case

the whole array has been divided into four bands with widths increasing in geometrical progression with a common ratio of 1.5. This will be clear from Table IV. The paints in the first band were classed as "very good," in the second band as "good," in the third band as "moderate," and the remainder as "bad." Marks of 3, 2, 1, and 0, respectively, were given to paints in the various classes. The merit figure has been derived by calculating the total score for each paint under the 10 different headings. Obviously the maximum possible figure is 30.

Finally, the paints were arrayed in order of decreasing merit figure. This array was again subdivided in the same manner and the paints in the respective bands have received the final classifications, "very good," "good," "moderate," and "bad."

The method of deriving the merit figures differs slightly from that used in previous work inasmuch as the paints are compared amongst themselves and not against an arbitrary selected standard, e.g., 10% of rusting. This alteration was desirable, not only because it renders the method consistent throughout, but also because the behaviour of the painting schemes as a whole is so markedly superior to that observed in previous tests that the use of the former standards of assessment would have proved insufficiently sensitive to distinguish clearly between the majority of the paints.

The merit figures of the paints deduced in this way are shown diagrammatically in Fig. 3. A

† The weighting factor for rusting has been increased to 10, as compared with 4 in the previous tests.

As stated later (see section C, sub-section (2)) in the case of the specimens that had been exposed to weathering in the as-rolled condition, a correlation was observed between the return for blistering and the percentage descaling of the surface at the time of painting. As the percentage descaling varied unavoidably to some extent from one specimen to another, the strict comparison of the index figures for different specimens in this surface condition is slightly invalidated. However, the specimens were selected at random and any possible effect on the final merit figure, deduced as described later in the text, is inappreciable at least in the case of the best paints to which chief interest is attached.

‡ Item A of section A, sub-section (8). In the previous tests, the comparison was based on the sum of items A and B, i.e., on the area over which the whole or part of the composite paint film was adherent.

§ Item D of section A, sub-section (8).

|| Paints Nos. 272-275 have been omitted from the statistical analysis because in the case of the first two the milling time was varied, whilst in that of paints Nos. 274 and 275, the surfaces to which they were applied were not strictly comparable with those used for the other paints. They have, however, been assigned "merit figures" on the same basis.

Pigments		Media	
AL	Aluminium	g	A
BC	Barium chromate		Modified phenol-formaldehyde/litho-oil
BLS	Basic lead sulphate	c	B
	Graphite	f	C
MB	Mineral black	k	Cammonne/litho-oil
RL	Red lead	a	D
WL	White lead	e	Alkyd/litho-oil/zinc-resinate
	Burnt/lead red	b	D
X	1 part, Barytes 1 part	x	G
ZC	Zinc chromate	q	Conpo-ester/litho-oil
ZH	Zinc	m	H
ZMO	Zinc oxide	j	100% phenolic-resins
ZNO	Zinc tetrahydro-chromate		Conpo-ester/litho-oil
	Note: The mixture RLI, WL2 is denoted by	r	100% phenolic-resins linseed-oil.
		v)	○ 25 Very good. ● 18 Good. ◻ 10 Moderate. ■ 4 Bad.

Fig. 4.—Correlation between Merit Figure and Total Paint Film Thickness. Basic Lead Sulphate Series.

few typical numerical data which illustrate the quantitative results will be found in Appendix B.

C.—DISCUSSION OF RESULTS.

(1) *Effect of Paint Film Thickness.*

Before proceeding to discuss the results of these tests, it should be remarked that in certain cases the film thickness of the painting scheme * has had an appreciable effect on performance. This is in apparent contrast with the results of the earlier tests described in the authors' previous paper, in which it was shown that the effect of the film thickness was insignificant in comparison with the influence of the variations in formulation. When, however, as in the present instance, the tests are concerned with groups of paints of essentially similar formulations, as regards both pigment and medium, the effects of film thickness become significant. It is obvious that the effect of film thickness requires further study and had the present researches not been carried out under war conditions greater consideration might have been given to this factor. As it is, it is hoped that the further investigations which will shortly be commenced by the Marine Corrosion Sub-Committee in collaboration with the Association of Ships' Composition Manufacturers (*see* section D, sub-section (2)) will serve to elucidate the subject.

This point is illustrated by Fig. 4 which is a plot of the results for all the paints of the basic lead sulphate series applied to specimens in strictly comparable surface conditions; the merit figure for each paint is shown in relation to the mean film thickness of the composite painting scheme on the two specimens to which it was applied. The general connection between the merit figure and the film thickness is unmistakable; a similar, but much less definite, correlation will be observed if the results for the paints of the zinc oxide series or those for the paints of the graphite and mineral black series be plotted in the same way. It should be noted, however, that the distinction in merit figure between the paints of the basic lead sulphate series, as a class, and those of the zinc oxide series, as a class, in which there is a major difference as regards pigmentation, is clear-cut and definite and independent of film thickness.

This question then arises when interpreting the results of these researches: Should the merit figures be taken as they stand or should some allowance be made for the possible effect of film thickness? The authors adhere to the attitude that they have consistently adopted since the

beginning of these investigations, namely, that the comparisons should be based on the paints as they are and not on what they might be. For instance, let us consider in detail the results for paints Nos. 232–235 and 154, in which the same pigmentation and medium has been used but in which the pigment/vehicle ratio has been varied. The merit figures of these paints are 1, 5, 9, 15, and 18, respectively, and the corresponding total film thicknesses are 112, 129, 135, 143, and 154 μ . This is as good a correlation between merit figure and film thickness as could be desired, but it is nevertheless largely of academic interest only.

Accordingly, although the authors pay due regard to the question of film thickness when this appears desirable, they will, in the main, accept and interpret the results as they are and without reference to this factor. The main purpose of this investigation is to deduce practicable paint formulations that may be relied upon to give good performance in service. This practical object will be most rapidly secured by concentrating on those paints that have been found to give good results and, although it is possible that the behaviour of some of the paints that have proved inferior in these tests might be improved by modifications in formulation leading to an increased film thickness when they are applied at the natural spreading rate, such developments are to be regarded as secondary to the main investigation.

(2) *Effect of Surface Condition before Painting.*

It will be recalled that each paint included in the tests was applied to two specimens and that, except in the case of paints Nos. 274 and 275, both the specimens had previously been weathered for the same period (either 6 or 2 months, according to the experimental series) but that one of them had been pickled before exposure to weathering, whereas the other was exposed with the mill scale in position. It therefore becomes of interest to compare the behaviour of the paints on these two types of surface.†

This comparison is made most simply by tabulating the number of cases in which one or other of the alternative surface preparations has given the better result in the case of each pair of specimens, judging by the various properties on which assessments of performance were based.‡ This has been done in Table V. With two apparent exceptions, namely, the *total index figure*, which will be discussed later, and the figures for rusting, in the case of the graphite and mineral

* As in the earlier tests, the average film thickness of each coat of paint applied to all the specimens has been calculated from the observed weight of wet paint and its formulation. For details of the method of calculation *see* F. Fancutt and J. C. Hudson, *loc. cit.*, p. 310 P.

† Both types of weathered specimens were cleaned by wire-brushing before painting, *see* section A, sub-section (4).

‡ *See* section B, sub-section (2).

TABLE V.—*Relative Performance of the Paints on As-rolled and Weathered and on Pickled and Weathered Surfaces.*

Series.	Basic Lead Sulphate.			Zinc Oxide.			Graphite and Mineral Black.		
Paint Nos.	149-200, 232-235, 272, and 273.			201-231.			236-271.		
Number of Paints.	53.			31.			36.		
	Better Results from,—			Better Results from,—			Better Results from,—		
	I. As-rolled and Weathered Specimen.	II. Pickled and Weathered Specimen.	No Difference.	I. As-rolled and Weathered Specimen.	II. Pickled and Weathered Specimen.	No Difference.	I. As-rolled and Weathered Specimen.	II. Pickled and Weathered Specimen.	No Difference.
Field Inspections.									
(i) Total index figure .	49	9	0	24	7	0	32	4	0
(ii) Index figure (rusting only) .	13	44	1	10	21	0	17	19	0
Laboratory Examination.									
(iii) Intact paint .	9	48	1	1	30	0	9	27	0
(iv) Rusting .	6	52	0	9	22	0	18	18	0
(v) Loss in weight .	8	47	3	1	30	0	5	31	0

black series, it is evident that the paints have behaved much better on the surfaces that were pickled before exposure to weathering than on those that were exposed to weathering in the as-rolled condition. It should be noted, however, that in the latter case the removal of the mill scale at the time of painting was incomplete * and it is possible that the behaviour of a steel plate that had been completely descaled by weathering before painting would not differ appreciably from that of a similar plate that had been pickled and then allowed to rust before painting. At the same time, it is clear that the former procedure is much less likely to achieve the desired result in a uniform manner within the limited weathering period imposed by practical conditions of ship-building. To prevent a misunderstanding, it should be added that the whole subject of the effect of the surface condition of the steel on the performance of underwater compositions is still obscure and is being studied by the Marine Corrosion Sub-Committee, but it has already been established that good results are not invariably obtained when paint is applied to a freshly descaled surface. On the whole, therefore, a weathering period after pickling may be regarded as beneficial rather than otherwise.†

The apparent anomaly between the results for the total index figure and the remaining observations (Table V.) is explained by the fact that the index figure is largely influenced by the returns for blistering. Fine blisters invariably form in a paint film over the areas where it lies on a previously rusted surface but no such blistering develops over

the areas where the paint lies over mill scale. As a result, the returns for blistering were considerably greater for the pickled and weathered specimens because the whole surface was rusted

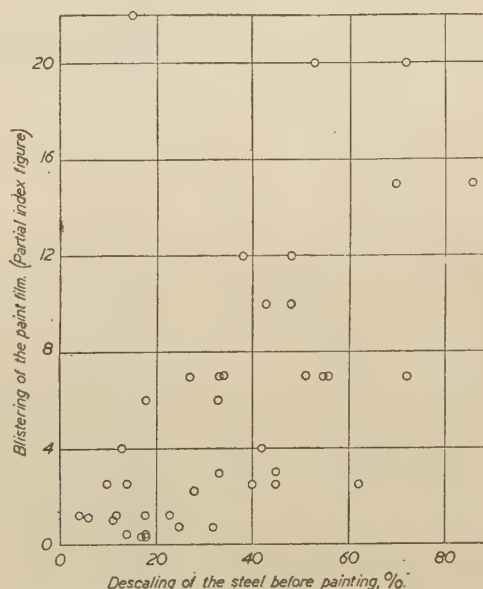


FIG. 5.—Correlation of Blistering of the Paint Film with Descaling of the Steel before Painting.

and capable of producing blisters whereas, in the case of the as-rolled and weathered specimens, no blistering occurred over the appreciable proportion of the surface from which the mill scale had not been removed by weathering.

* See Table II.

† This is in marked contrast to the behaviour of paints applied to steel subsequently exposed to atmospheric corrosion, where the ideal procedure is to apply the paint immediately after descaling.

This last matter has been carried further and it has been shown by statistical methods that there is a correlation between the index figure for blistering, as observed in the early inspections at Caernarvon, and the extent to which the as-rolled and weathered specimens had shed their mill scale before painting. This is illustrated by Fig. 5 which shows graphically the relation between

these two variables in the case of 40 of the as-rolled and weathered surfaces, selected at random, that were coated with paints of the basic lead sulphate or of the zinc oxide series. In this case the correlation coefficient (Spearman) is 0.735. It follows as a corollary that comparative tests on different paints such as these are best made on specimens from which the mill scale has been

TABLE VI.—*List of Paints Graded as "Very Good."*

Merit Figure.	Paint.		Formulation.	Medium.	Storage Properties.†	
	No.	Code.	Pigment,* parts by weight.		Room Temperature.‡	120° F.
28	174	<i>cbx</i> 212/ <i>B</i>	Basic lead sulphate 2 White lead 1 Extender 2	<i>B</i> Coumarone/litho-oil	<i>S</i>	<i>Xs, p</i>
	189	<i>cgx</i> 212/ <i>E</i>	Basic lead sulphate 2 Aluminium 1 Extender 2	<i>E</i> Chlorinated rubber	<i>Xg</i>	<i>Xg</i>
27	163	<i>cqx</i> 212/ <i>E</i>	Basic lead sulphate 2 Zinc chromate 1 Extender 2	<i>E</i> Chlorinated rubber	<i>Xg</i>	<i>Xg</i>
26	177	<i>cbx</i> 212/ <i>E</i>	Basic lead sulphate 2 White lead 1 Extender 2	<i>E</i> Chlorinated rubber	<i>Xg</i>	<i>Xg</i>
25	155	<i>cnx</i> 211/ <i>B</i>	Basic lead sulphate 2 Barium chromate 1 Extender 1	<i>B</i> Coumarone/litho-oil	<i>S</i>	<i>Xs, p</i>
	186	<i>cgx</i> 212/ <i>B</i>	Basic lead sulphate 2 Aluminium 1 Extender 2	<i>B</i> Coumarone/litho-oil	<i>S</i>	<i>p</i>
	215	<i>jqx</i> 211/ <i>E</i>	Zinc oxide 2 Zinc chromate 1 Extender 1	<i>E</i> Chlorinated rubber	<i>S</i>	<i>Xg</i>
24	193	<i>cgx</i> 421/ <i>A</i>	Basic lead sulphate 4 Aluminium 2 Extender 1	<i>A</i> Modified phenol-formaldehyde/litho-oil	<i>S</i>	<i>p</i>
	197	<i>cmx</i> 211/ <i>B</i>	Basic lead sulphate 2 Zinc 1 Extender 1	<i>B</i> Coumarone/litho-oil	<i>S</i>	<i>p</i>
23	185	<i>cgx</i> 212/ <i>A</i>	Basic lead sulphate 2 Aluminium 1 Extender 2	<i>A</i> Modified phenol-formaldehyde/litho-oil	<i>S</i>	<i>S</i>
22	216	<i>jqx</i> 211/ <i>F</i>	Zinc oxide 2 Zinc chromate 1 Extender 1	<i>F</i> 100% phenolic-resin/tung-oil/linseed-oil	<i>S</i>	<i>S</i>
25	274 §	<i>cbx</i> 212/ <i>H</i>	Basic lead sulphate 2 White lead 1 Extender 2	<i>H</i> 100% phenolic-resin/linseed-oil	<i>S</i>	<i>Xs</i>

* The "extender" consists of equal parts by weight of Burntisland red and barytes.

† The period of storage was approximately 6 months. The symbols used are as follows: *S*, satisfactory; *X*, needs improvement; *g*, gelled; *p*, gas pressure developed; and *s*, hard settlement.

‡ About 70° F.

§ This paint is not strictly comparable with the others because one of the specimens to which it was applied was shot-blasted instead of being weathered, and the other was pickled, but weathered for 2 months instead of 6.

removed before weathering unless special precautions are taken to ensure that the degree of descaling is reproducible from one specimen to another.

(3) *Basic Lead Sulphate Series and Zinc Oxide Series.*

(a) *The Best Anti-Corrosive Paints.*

It will be advantageous to consider the paints of the basic lead sulphate series and of the zinc oxide series together. According to the method of classification adopted, 11 of the 87 paints concerned are included in the category "very good." A short list of these paints is given in Table VI.

The merit figures of the "very good" paints range from 28 to 22.* Clearly, differences of one or two units in the merit figure have little significance and it may be purely a matter of chance that other paints at the head of the next division ("good") fail to qualify for inclusion in this group; moreover, no great importance can be attached to the relative positions of the paints included in Table VI. It may, however, be noted, as affording a standard of comparison with the previous tests, that paint No. 173 (*cbx* 212/*A*) has a merit figure of 17 ("good") and does not appear in the short list. This paint is pigmented with 2 parts of basic lead sulphate, 1 part of white lead, and 2 parts of extender, and is in the modified phenol-formaldehyde/litho-varnish medium *A*. Except for the facts that the extender pigment now consists of equal parts of Burntisland red and barytes instead of wholly of the former, and that a litho oil was used for the preparation of the medium instead of a stand oil, this paint corresponds with paint No. 32, which was chosen as the most practicable of the best of the 85 paints tested at Caernarvon in the earlier series. In the present tests there are 18 other paints with merit figures of 17 or more, *i.e.*, that are equal to or better than paint No. 173 in protective properties.

Detailed study of the formulation of the 11 "very good" paints listed in Table VI. gives rise to the following points:

(i) *Pigmentation.*—Nine paints belong to the basic lead sulphate series, but only two to the zinc oxide series. Basic lead sulphate occurs in admixture with barium chromate, zinc chromate, white lead, aluminium, and zinc, but not with zinc tetrahydroxy-chromate or red lead. The only pigment giving "very good" results in combination with zinc oxide is zinc chromate.

(ii) *Medium.*—Four paints are in medium *E*, chlorinated rubber (out of four paints made for test

in this medium); four (out of ten made) are in medium *B*, coumarone litho oil; two (out of 43) are in medium *A*, modified phenol-formaldehyde/litho-oil; and one (out of four) is in medium *F*, 100% phenolic-resin/tung-oil/linseed-oil. No paint in medium *C*, alkyd/litho-oil/zinc-resinate, medium *D*, Congo-ester/litho-oil/zinc-resinate, or medium *G*, Congo-ester/litho-oil, occurs in the short list, but medium *H*, 100% phenolic-resin/linseed-oil, would have been represented by paint No. 274 (*cbx* 212/*H*) had not this paint been omitted from Table VI. for the reason already given.

It is an interesting fact that the two "very good" paints in medium *A* (modified phenol-formaldehyde/litho-oil), namely, Nos. 193 (*cgx* 421/*A*) and 185 (*cgx* 212/*A*), are both pigmented with basic lead sulphate, aluminium, and extender. This is a welcome confirmation of the observation that the prototype paint of this sub-series, No. 58 (*ceg* 832), was one of the three best paints in the earlier series of tests. As already stated, paint No. 32 (*cbd* 212) was recommended for practical use at that time in preference to paint No. 58, but this was because the latter contains aluminium, then in short supply.

(b) *Effect of the Pigment.*

(i) The most striking fact that emerges from a study of Fig. 3 is the marked superiority of the paints of the basic lead sulphate series to those of the zinc oxide series. Of the 28 paints classed as "very good" or "good," only two contain zinc oxide, *viz.*, paints Nos. 215 (*jgx* 211/*E*) and 216 (*jgx* 211/*F*) which consist of mixtures of zinc oxide, zinc chromate, and extender in medium *E* (chlorinated rubber) and medium *F* (100% phenolic-resin/tung-oil/linseed-oil), respectively. Apart from these two paints and five others that were classed as "moderate," all the paints containing zinc oxide were classed as "bad."

It would seem fair to conclude that, in general, basic lead sulphate is a much better pigment for all-round use in underwater paints than is zinc oxide. This does not mean that satisfactory paints cannot be formulated with a zinc oxide pigmentation, but the range of media included in the present investigation is fairly wide and it seems certain that zinc oxide is a much less adaptable pigment for this purpose than basic lead sulphate.

(ii) Of six pigmentation systems studied in the basic lead sulphate series,† that incorporating zinc tetrahydroxy-chromate has proved the least satisfactory. Similarly, in the zinc oxide series, zinc tetrahydroxy-chromate has given no better results than barium chromate and it has proved markedly inferior to zinc chromate. It may be

* If judged by the same standards, paint No. 274 (*cbx* 212/*H*) would have a merit figure of 25; see footnote § to Table VI.

† The system incorporating red lead contains only two paints and is omitted from the comparison.

added, as will be discussed later in section C, sub-section (4), that, in the case of the graphite and mineral black series, zinc tetrahydroxy-chromate has given the worst results of all the five inhibitors tested.

Thus it will be seen that the present series of tests has failed to produce any evidence that zinc tetrahydroxy-chromate, as used in the formulations detailed in Appendices A and B, is a more valuable constituent of anti-corrosive compositions than the more usual chromate pigments. It is, however, desirable to treat these results with caution, owing to the somewhat lower film thicknesses of the paints incorporating zinc tetrahydroxy-chromate, and it is pertinent to add that this pigment was originally suggested as suitable for incorporation in priming paints based on ordinary linseed-oil media.

(iii) In the case of tests on paints in medium *A* (modified phenol-formaldehyde/litho-oil), particular attention was paid to pigment combinations based on basic lead sulphate in admixture with zinc chromate, white lead, or aluminium, respectively, because paints of all three types of pigmentation had given promising results in the earlier tests. The further test results now available tend to show that in this type of formulation zinc chromate is inferior to the other two secondary pigments mentioned. On the whole, the basic lead-sulphate/aluminium/extender combination has proved the best. In the cases in which the relative proportions of the ternary pigment mixture are the same for all three systems in medium *A*, this pigment combination has yielded two "very good" paints, two "good" ones, and one "moderate" one; the "score" for basic-lead-sulphate/white-lead/extender is five "good" paints and that for basic-lead-sulphate/zinc-chromate/extender is one "good" paint and four "moderate" ones.

It is probable, therefore, that the judicious addition of aluminium to paints pigmented with basic lead sulphate will lead to enhanced protective properties; it may also be added that there is some evidence from the storage trials that such additions increase the package stability of the paints. Fig. 3 points to the conclusion that there is no advantage in increasing the ratio of aluminium to basic lead sulphate beyond 1 part to 2 parts by weight.

(iv) Detailed study of the results for individual paints in medium *A* (modified phenol-formaldehyde/litho-oil) shows that the merit figure is not markedly sensitive to differences in the proportions of the individual pigments in the mixtures. No pronounced effect of extender additions, such as was reported in the earlier series of tests, has been observed except, possibly, in the case of paints Nos. 170 (*cax* 212/*A*) and 172 (*cbx* 214/*A*). In all probability this is because the percentage

of extender in the paints exceeds 40% by weight in only two cases and is generally less; moreover, one half of the extender by weight consists of Burntisland red. It is probable, therefore, that in the great majority of cases the critical extender content has not been exceeded.

(v) In the basic lead sulphate series, barium chromate gave the best results of the three chromate pigments. This pigment was not tested in medium *E* (chlorinated rubber) or medium *F* (100% phenolic-resin/tung-oil/linseed-oil) but it gave "good" or "very good" results in combination with basic lead sulphate when incorporated, respectively, in medium *A* (modified phenol-formaldehyde/litho-oil) or medium *B* (coumarone/litho-oil).

(c) *Effect of the Medium.*

The effect of differences in the paint medium is best studied from Fig. 6 which illustrates diagrammatically the results of the tests in all cases in which a given pigment mixture was bound in more than one medium. A differentiation is made in this diagram between the performance of the paints on the as-rolled and weathered and on the pickled and weathered specimens, respectively. The partial merit figure for the former (maximum value 15) is shown in the upper half of the ring and that for the latter in the lower half of the ring. The figure in the central circle is the sum of these two figures and is the merit figure for the paint, as defined in section B, sub-section (2), and shown in Fig. 3.

It will be recalled that four pigment combinations (*cqx* 212, *cbx* 212, *cgx* 212, and *jcx* 211) were common to all seven media. The merit figures for each set of four paints added together may serve to give a general idea of the relative performances of these media in these particular tests. This has been done in Table VII, from which it is clear that :

(i) The paints in medium *E* (chlorinated rubber) are superior to all the others. This was evident at each visual inspection throughout exposure. At the final examination, after the specimens had been cleaned, the whole of the paint films in this medium were found to be perfectly intact up to and including the edges, and there was little evidence of deterioration. All four chlorinated-rubber paints "gelled" in the storage tests, so that their properties in this respect need improvement.

(ii) The next medium in order of merit is medium *B* (coumarone/litho-oil). Particularly good results were obtained with four paints of the basic lead sulphate series in this medium, namely, paints Nos. 155 (*cnx* 211/*B*), 174 (*cbx* 212/*B*), 186 (*cqx* 212/*B*), and 197 (*cmx* 211/*B*).

In the zinc oxide series, this coumarone medium was the most satisfactory of the four media, *A*, *B*, *C*,

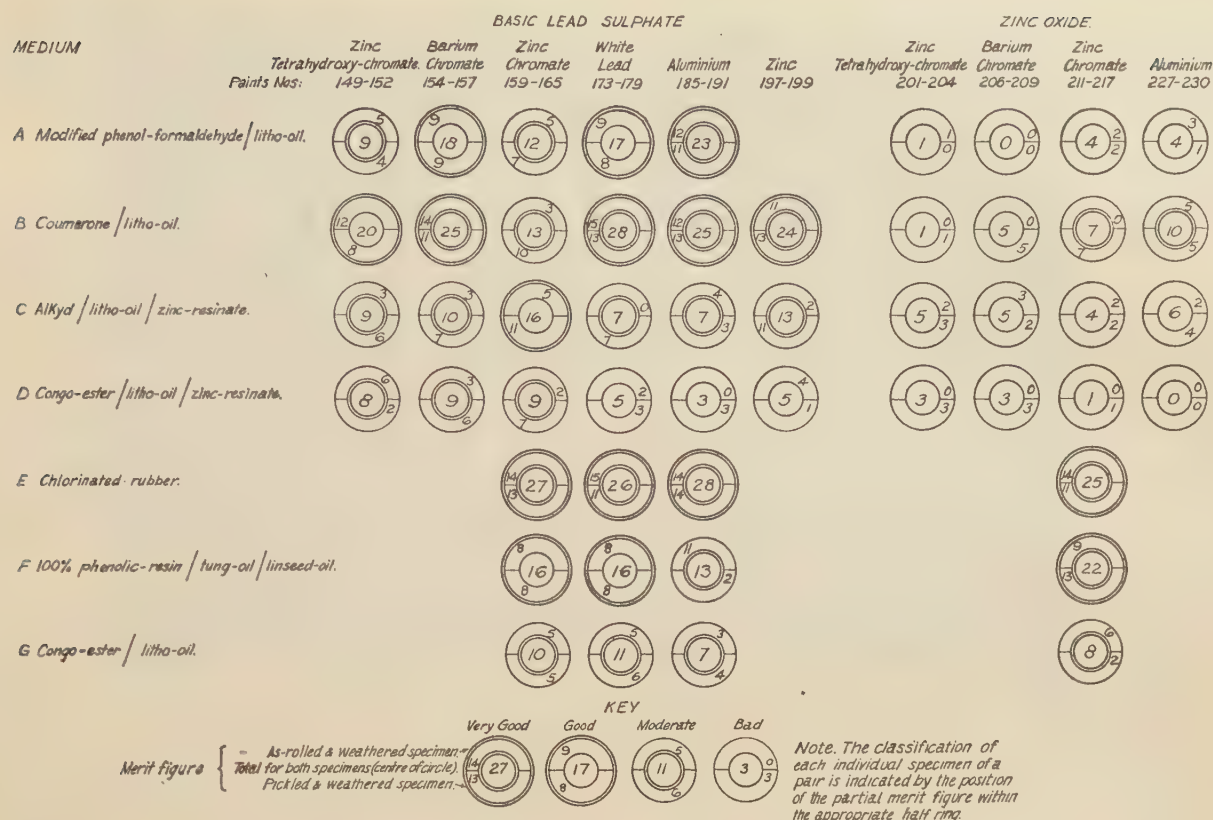


FIG. 6.—Comparison of the Different Media.

TABLE VII.—Merit Figures for the Pigment Formulations Common to All Seven Media.

Reference.	Medium.	Pigmentation.				Total.
	Description.	cxz 212.	cbz 212.	cxz 211.	jgz 211.	
A	Modified phenol-formaldehyde/litho-oil	12	17	23	4	56
B	Coumarone/litho-oil	13	28	25	7	73
C	Alkyd/litho-oil/zinc-resinate	16	7	7	4	34
D	Congo-ester/litho-oil/zinc-resinate	9	5	3	1	18
E	Chlorinated rubber	27	26	28	25	106
F	100% phenolic-resin/tung-oil/linseed-oil	16	16	13	12	57
G	Congo-ester/litho-oil	10	11	7	8	36
	Total	103	110	106	61	380

and D, tested with more than one pigment combination. Of the 16 paints concerned, two were rated as "moderate" and both of these were in medium B (coumarone/litho-oil). It should be noted that the oil length of medium B is shorter than that of medium A (modified phenol-formaldehyde/litho-oil), namely, 1 : 1 as compared with 2 : 1.*

(iii) There is no significant difference between the aggregate merit figures for the four paints formulated both in medium A (modified phenol-formaldehyde/litho-oil) and in medium F (100% phenolic-resin/tung-oil/linseed-oil), but this is due

to the much better performance of the zinc-oxide/zinc-chromate/extender combination in the 100% phenolic-resin medium. In the case of the three paints of the basic lead sulphate series the advantage lies on the whole with medium A (modified phenol-formaldehyde/litho-oil). It would seem that the 100% phenolic-resin medium used is particularly suitable for formulations incorporating zinc oxide, in which connection it may be noted that some of the most successful American anti-corrosive paints are in this type of medium and pigmented with mixtures containing zinc oxide and zinc chromate.

* See Appendix A.

(iv) Paints in medium *A* (modified phenol-formaldehyde/litho-oil) gave good results when pigmented with mixtures of basic lead sulphate with barium chromate, white lead, or aluminium, plus extender in all cases. Paint No. 171 (*cax* 211/*A*) pigmented with basic lead sulphate, red lead, and extender was also rated as "good"; this pigment mixture was only tested in medium *A*.

(v) The remaining three media shown in Fig. 6 and listed in Table VII. are distinctly inferior to the preceding ones. There is little to choose between medium *C* (alkyd/litho-oil/zinc-resinate) and medium *G* (Congo-ester/litho-oil). The former has given a good result when pigmented with the basic-lead-sulphate/zinc-chromate/extender combination.

(vi) Medium *D* (Congo-ester/litho-oil/zinc-resinate) is the least satisfactory of all and is inferior to medium *G* (Congo-ester/litho-oil) which is essentially of the same type but without the addition of zinc resinate.

(vii) Although the surface conditions of the specimens to which paints Nos. 274 and 275 in medium *H* (100% phenolic-resin/linseed-oil) were applied differed from those of the other specimens of these series,* it is noteworthy that paint No. 274 (*cbx* 212/*H*) in which this medium is pigmented with basic lead sulphate, white lead, and extender would be classed as "very good" if judged by the same standards. On the other hand, paint No. 275 (*jgx* 211/*H*) pigmented with zinc oxide, zinc chromate, and extender would be rated as "bad."

(d) Effect of the Pigment/Vehicle Ratio.

It is recognized that variations in pigment/vehicle ratio have a marked influence on the protective properties and so from some points of view it would be desirable to test each combination of pigment and medium at several different pigment/vehicle ratios. Unfortunately, the effect of this procedure would be to increase the volume of work involved to an impracticable degree,† so that, as already stated, in the present investigation it has been considered preferable to select the pigment/vehicle ratio in each case on the basis of experience coupled with experimental determinations of the oil absorption of the pigments.

It is obvious that this wide subject cannot be adequately disposed of by the few simple tests on one sub-series of paints, Nos. 154 (*cnx* 211/*A*) and 232–235, in which the pigment/vehicle ratio was deliberately varied. Yet it is satisfactory to

record that the results shown in Fig. 3 indicate that, in this case at least, the pigment/vehicle ratio selected for the master paint, No. 154, seems to have been reasonably near the optimum value.

(e) Effect of Milling Time.

Two other paints, Nos. 272 and 273, were made with the same formulation as paint No. 168 (*eqx* 122/*A*) but their milling time was varied. Whereas paint No. 168 was ball-milled for 12 hr., the milling time was increased to 24 and 72 hr., respectively, for paints Nos. 272 and 273. The corresponding merit figures of the paints in this order are 7, 3, and 7, from which it may be concluded that differences in milling time have had no marked effect in this particular case. Obviously, to investigate the matter thoroughly it would be necessary to conduct similar tests on a greater number of paints.

(4) Graphite and Mineral Black Series.

Reference to Fig. 3 will show that the tests on the graphite and mineral black series of paints have failed to produce the anticipated results, in so far as it has not been found that increasing proportions of inhibitor in the pigment mixture have had any marked effect on the merit figure of the paints. The explanation for this may be that graphite can hardly be classed as an inert pigment and that different results might have been obtained if the basis mixture to which the inhibitors were added had been neutral, *e.g.*, a mixture of mineral black and red oxide. Nevertheless, the tests have had at least one valuable result in that they again confirm the marked benefits to be gained from the use of basic lead sulphate as a constituent of anti-corrosive paints, at least when bound in a modified phenol-formaldehyde/litho-oil medium.

TABLE VIII.—Average Merit Figures for the Paints of the Graphite and Mineral Black Series.

Inhibitor.		Average Merit Figure.	
		8 Paints.	4 Paints.
<i>r</i>	Zinc tetrahydroxy-chromate	...	4.8
<i>n</i>	Barium chromate	7.8	9.3
<i>q</i>	Zinc chromate	13.0	14.8
<i>v</i>	Red lead, 1; white lead, 2	6.5	5.0
<i>c</i>	Basic lead sulphate	17.0	15.0

It will be seen from Table VIII. that the average merit figure of the eight paints formulated with

* In the case of paints Nos. 274 and 275, owing to shortage of materials, specimens prepared by shot-blasting were substituted for the as-rolled and weathered specimens. The second specimen of each pair was prepared in the normal manner, by pickling followed by weathering for 2 months.

† In the present tests the painting and immersion of the specimens alone occupied 120 man-days.

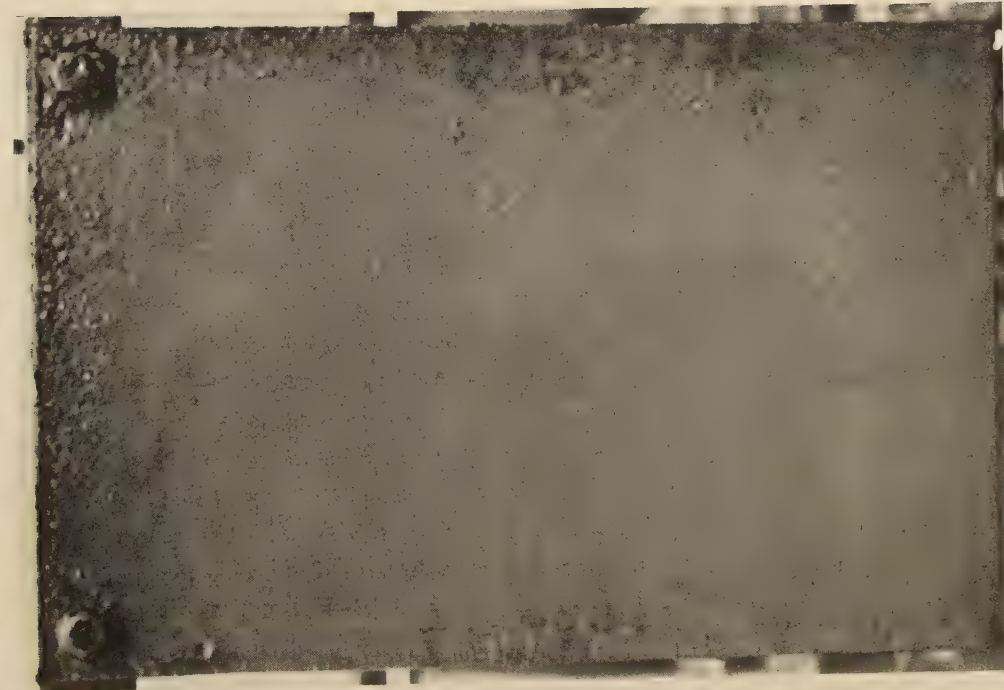


FIG. 7(a).—Two Coats of Paint No. 173, one Coat of Paint No. 4F10/43.



FIG. 7(b).—Control Three-Coat Proprietary Painting Scheme. The Both specimens were in the as-rolled and weathered condition before painting. The photographs were taken while they were wet.



FIG. 8(b).—Specimen B, primed with a proprietary anti-corrosive paint. (Both specimens were prepared for painting by immersion in sea-water for 1 month and the painting was completed by the application of two further coats of the proprietary anti-corrosive paint and anti-fouling composition, respectively. The specimens had been immersed at Caernarvon for 31 weeks when the photographs were taken and were wet at the time.)

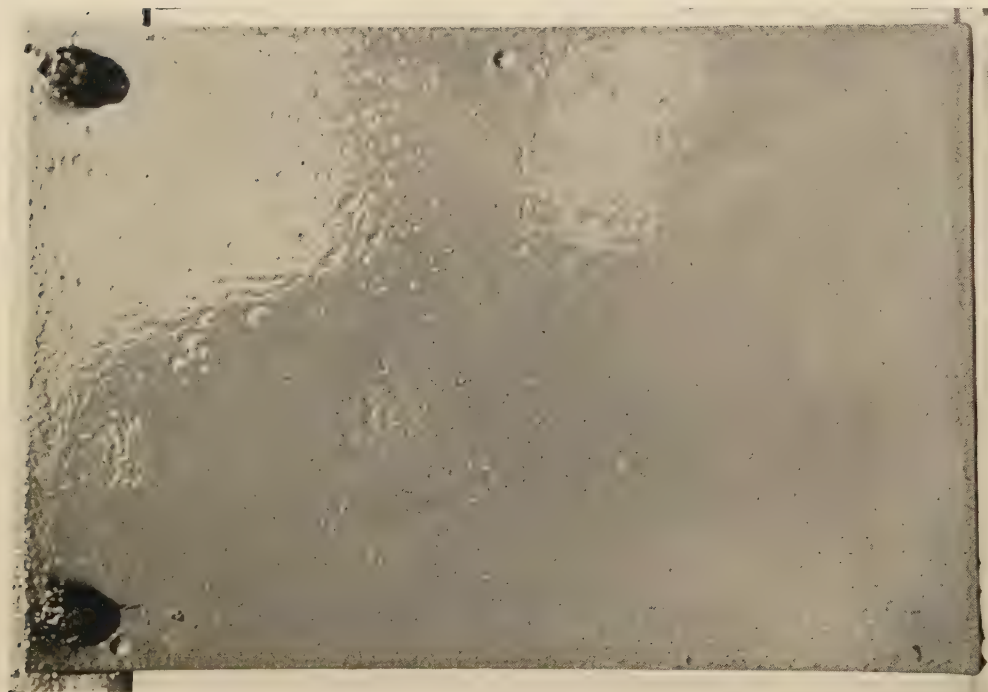


FIG. 8(a).—Specimen A, primed with Paint No. 32.

FIG. 8.—Value of Paint No. 32 as a Primer for Underwater Painting Schemes. (Both specimens were prepared for painting by immersion in sea-water for 1 month and the painting was completed by the application of two further coats of the proprietary anti-corrosive paint and anti-fouling composition, respectively. The specimens had been immersed at Caernarvon for 31 weeks when the photographs were taken and were wet at the time.)

basic lead sulphate, zinc chromate, barium chromate, and with the mixture of red lead and white lead (1:2), respectively, decreases in this order. Zinc tetrahydroxy-chromate was only incorporated in four paints, but if the average merit figures for corresponding groups of four paints are taken, it will be found that this pigment has given the worst results of all, its average merit figure of 4.8 being slightly, if not significantly, inferior to that of 5.0 for the red lead and white lead mixture.

It may be noted, without going into detail, that the effect of the surface condition of the specimens was more pronounced in the paints of this series than in those of the basic lead sulphate and zinc oxide series. Whereas the correlation coefficient between the respective orders of merit of the latter paints on as-rolled and weathered and on pickled and weathered specimens is 0.70, in the case of the graphite and mineral black paints it is only 0.35.*

D.—CONCLUSIONS.

(1) *General Standard of Performance of the Formulated Anti-Corrosive Paints.*

The method adopted in this communication of presenting the results has one drawback: The merit figure conveys no immediate indication of the absolute performance of the formulated anti-corrosive paints as they are compared amongst themselves throughout. A few additional facts are therefore given which may be of assistance to those who wish to assess the practical significance of the results obtained.

(a) *Comparison with a Control Proprietary Painting Scheme.*

Duplicate specimens with similar surface conditions to those used for testing the paints of the basic lead sulphate and the zinc oxide series were painted with a three-coat proprietary system of Admiralty quality compositions (two coats of anti-corrosive, one coat of anti-fouling paint) which, in previous tests by the Marine Corrosion Sub-Committee, had proved to be well above the average for commercial compositions of this type. These control specimens were prepared and immersed simultaneously with those coated with the formulated paints and were subjected to the same inspections throughout exposure and at the conclusion of the test. The merit figure of the proprietary scheme, calculated by the standards already described, was 6, *i.e.*, on the classification used for the formulated paints it would have been graded as "bad." Inspection of the results

shows that 56 of the 87 paints included in the basic lead sulphate series and in the zinc oxide series have a higher merit figure than this. Indeed, if the comparison is restricted to paints of the more satisfactory basic lead sulphate series, only seven out of 56 paints proved inferior to the control and two of these were deliberately formulated with an abnormal pigment/vehicle ratio.†

In fairness to the proprietary composition it should be noted that the spreading rates of its constituent coats were appreciably greater than in the case of the formulated paints‡ and therefore the thickness of the composite paint film was correspondingly less, but this seems to be a fairly general characteristic of commercial ships' bottom compositions. Some indication of the behaviour of the formulated painting schemes in relation to that of the proprietary control will be gathered from Fig. 7.

(b) *General Comparison of Formulated Paints with Commercial Ships' Bottom Compositions.*

In connection with an investigation commenced at Emsworth by Dr. I. G. Slater and continued at Millport by Mr. K. A. Pyefinch, the object of which was to elucidate the effect on the results of conducting paint tests on new steel as compared with painting over an old painted steel surface, the opportunity was taken to compare painting schemes based on paints Nos. 173 (*cbx 212/A*), 174 (*cbx 212/B*), and 178 (*cbx 212/F*) with 24 proprietary painting schemes, using samples taken from H.M. Dockyard stock.

Each painting scheme was tested in quadruplicate, being applied to two old specimens previously used for raft tests (wherever possible of the same paint) and to two new specimens, prepared by pickling to remove the mill scale and weathering in the atmosphere for 30 days, with the usual wire-brushing. Two coats of anti-corrosive paint were applied, followed by a final coat of the same make of anti-fouling composition; the formulated anti-fouling composition AF10/43 was used over the formulated anti-corrosive paints.

Details of the test, which was conducted on essentially the same lines as the present investigation, need not be given here. The pertinent fact is that in the final ranking order, as regards protective qualities, the formulated painting schemes were classed as follows, the total number of schemes tested being 27:

Paint No.	Freshly Weathered Steel.	Old Painted Steel.
173 (<i>cbx 212/A</i>)	4th	3rd
174 (<i>cbx 212/B</i>)	10th	18th
178 (<i>cbx 212/F</i>)	2nd	2nd

* The comparison between the different paints of the graphite and mineral black series is not, of course, invalidated, as they have all been tested on comparable surfaces as regards the respective members of the pair of specimens painted with each.

† Paints Nos. 272 to 274 are omitted from these comparisons.

‡ See Table X.

In this particular test, paint No. 174 in medium *B* (coumarone/litho-oil) has fallen somewhat from grace and no excuse is made for this, but it is evident that paint No. 173 in medium *A* (modified phenol-formaldehyde/litho-oil) and paint No. 178 in medium *F* (100% phenolic-resin/tung-oil/linseed-oil) have proved superior to all but one (or in the former case all but two or three) of the wide range of commercial compositions tested, both when applied to new steel and when applied to an old surface already painted.

(c) *Value of Paint No. 32 as a Primer for New Steel.*

Another series of tests was undertaken at Caernarvon at the request of the Director of Merchant Shipbuilding, with a view to ascertaining the most efficient method of painting the bottoms of new constructions. Comparisons were made between the results obtained by using different priming coats under commercial bottom compositions of wartime *C/Q* and *M.O.W.T.* qualities.* It was found that when a single coat of priming paint was applied to new steel and the painting was completed by the application of one anti-corrosive coat followed by one anti-fouling coat of commercial bottom compositions of the qualities indicated, much better results were obtained by using paint No. 32 (*cbd* 212) † as the priming coat than by the use of a red oxide primer,‡ a mixed red and white lead primer,§ or by the application of an additional coat of the same brand of anti-corrosive paint. This last fact is illustrated by Fig. 8. The specimens shown in this illustration were prepared for painting by weathering in sea-water for one month, followed by wire-brushing, and washing in fresh water; this accounts for the pitted appearance of the specimen in Fig. 8(a). When dry, specimen *A* was given a priming coat of paint No. 32 but specimen *B* was primed with a proprietary anti-corrosive paint. Thereafter, the painting was completed in both cases by the application of a second coat of the proprietary anti-corrosive paint, followed by a finishing coat of the corresponding proprietary anti-fouling composition. The photographs were taken after the specimens had been immersed for 31 weeks at Caernarvon; when examined, specimen *A* (primed with paint No. 32) was found to be in perfect condition.

(2) *Future Developments.*

These comparisons between the formulated paints developed by the Marine Corrosion Sub-Committee and the general run of proprietary compositions should not be misinterpreted. They

are not made with any intention of decrying the latter, many of which have given satisfactory results under practical conditions over a number of years, but rather with a view to demonstrating, in the case of anti-corrosive paints at least, that even better formulations are possible if users are prepared to purchase on the basis of performance values rather than on that of price alone.

Clearly the formulations given in this paper may need slight modification for practical purposes, particularly, perhaps, for use in dry dock where rapidity of drying is a paramount consideration, but they should be capable of application as they stand for the initial painting of new ships on the stocks, which is the most important part of the ship's history so far as protection of the bottom plates is concerned. The authors have pleasure in recording that, as a result of negotiations between the Marine Corrosion Sub-Committee and the Association of Ships' Composition Manufacturers, further investigations of ships' bottom compositions, at least in the case of anti-corrosive paints, will proceed on a collaborative basis, and they look forward to a fruitful outcome of such collaboration, both as regards fundamental and practical knowledge in this field.

It has already been stated that 18 of the paints tested have merit figures better than or equal to that of paint No. 173 (*cbx* 212/*A*). The use of this paint itself would establish a good standard of performance for a protective paint. The choice between it, the 18 paints of equal or higher ranking in the present order of merit, and any further paints of corresponding or better performance that may be developed, will largely be governed by consideration of relative cost and properties of the paints other than corrosion resistance proper. Consequently, the most fruitful line of advance would now appear to consist in conducting as many practical tests as possible on actual ships' bottoms. These tests alone can give a final indication of the merits of the paints and cannot fail to bring to light any respects in which they need further improvement.

ACKNOWLEDGMENTS.

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* These abbreviations denote standard qualities of anti-corrosive and anti-fouling compositions, respectively, adopted by the Ministry of War Transport for use on merchant shipping during the war.

† Paint No. 32 was the prototype of paint No. 173 (*cbx* 212/*A*) (see section C, sub-section (3)).

‡ Primer of good quality and ground in linseed oil.

specimens of steel plate for test purposes, to Bakelite, Ltd., for the provision of 100% phenolic-resin media, and to the Harbour Master and Trustees of the Port of Caernarvon for affording mooring facilities at that port.

The authors gladly acknowledge the support and encouragement received from the late Chairman, Dr. G. D. Bengough, F.R.S., his successor, Professor J. E. Harris, and the other members of the Marine Corrosion Sub-Committee. Amongst the latter, special mention is due to Dr. I. G. Slater, of the Admiralty Metallurgical Laboratory, Emsworth, who seconded two members of his staff, Mr. A. Catherall and Mr. A. Partington, to assist with the painting and immersion of the specimens. Similar assistance was rendered by Dr. T. A. Banfield and Dr. G. L. Wild, of the Corrosion Committee Staff. Mr. F. G. Dunkley and Mr. D. G. Soar, of the Paint Laboratory, London, Midland, and Scottish Railway Company, assisted with the formulation and preparation of the paints, and the inspections on the raft were made by Dr. Banfield and Dr. Wild, the former being responsible for the final examination of the specimens. Assistance in the computation of the results has been rendered by Mr. G. P. Acock, of the Corrosion Committee Staff.

APPENDIX A.—Formulation and Method of Manufacture of the Different Media.

Details of the formulation and method of manufacture of the media used in this investigation are given below. All compositions are stated in percentage by weight.

Medium A (Modified Phenol-Formaldehyde/Litho-Oil).

Modified phenol-formaldehyde resin (Bedesol 66)	21.25
Heavy litho oil	42.50
Naphtha	35.40
Lead naphthenate (Pb 24%)	0.68
Cobalt naphthenate (Co 6%)	0.17

Sp. gr., 0.948 at 70° F. Viscosity, 5.7 poises at 70° F.

Method.—Heat 20% of oil to 120° C. and add resin gradually as temperature rises to 180° C. Increase temperature to 250° C. and add remaining oil slowly, holding at this temperature for 1 hr. Cool to 180° C., thin, and add driers.

Medium B (Coumarone/Litho-Oil).

Coumarone resin (Epok C.46)	29.4
Heavy litho oil	29.4
Naphtha	40.8
Lead naphthenate (Pb 24%)	0.4

Sp. gr., 0.970 at 70° F. Viscosity, 1.7 poises at 70° F.

Method.—Heat resin and oil together to 180° C., then thin, and add driers.

Medium C (Alkyd/Litho-Oil/Zinc-Resinate).

Alkyd resin (Paralac 18)	10.8
Varnish linseed-oil	5.4
Heavy litho oil	27.0
Zinc resinate	4.9
Naphtha	46.6
Lead naphthenate (Pb 24%)	4.4
Cobalt naphthenate (Co 6%)	0.9

Sp. gr., 0.936 at 70° F. Viscosity, 2.9 poises at 70° F.

Method.—Heat resin and varnish linseed-oil to 265° C. until bright. Add litho oil gradually at this temperature, keeping mixture bright throughout. Heating time should be approximately 2 hr. Cool to 180° C., thin, and add driers and zinc resinate in solution.

Medium D (Congo-Ester/Litho-Oil/Zinc-Resinate).

Congo ester	10.6
Heavy litho oil	31.8
Zinc resinate	4.6
Naphtha	48.3
Lead naphthenate (Pb 24%)	4.2
Cobalt naphthenate (Co 6%)	0.5

Sp. gr., 0.928 at 70° F. Viscosity, 3.9 poises at 70° F.

Method.—Heat 20% of oil and all the resin to 260° C. When clear, add remaining oil gradually, keeping at 260° C. Cool to 180° C., thin, and add driers and zinc resinate in solution.

Medium E (Chlorinated Rubber).

(a) Chlorinated rubber	25.2
Amyl acetate	8.4
Xylene	66.4
(b) Cereclor	73.5
Xylene	26.5

Note.—The paints in this medium were prepared by grinding the pigment with a mixture of 2 parts by weight of (b) and 1 part by weight of (a) in a cone mill, afterwards adding the requisite quantity of (a) to give a chlorinated-rubber/Cereclor ratio of 1:1.

Medium F (100% Phenolic-Resin/Tung-Oil/Linseed-Oil).

100% phenolic resin (Bakelite No. R.254)	21.5
Tung-oil	21.1
Varnish linseed-oil	20.9
White spirit	26.1
Xylene	5.4
Dipentene	5.0

Sp. gr., 0.938 at 70° F. Viscosity, 3.9 poises at 70° F.

Method.—Raise temperature of varnish linseed-oil and of half the resin to 293° C. in $\frac{1}{2}$ hr. and hold to a long string. Check with remainder of resin, dissolve, and add tung-oil. Raise temperature to 240° C. and hold for about $\frac{1}{2}$ hr. to a heavy drip from paddle. Cool and thin.

Medium G (Congo-Ester/Litho-Oil).

Congo ester	12.8
Heavy litho oil	38.4
Naphtha	43.2
Lead naphthenate	5.0
Cobalt naphthenate	0.6

Sp. gr., 0.932 at 70° F. Viscosity, 4.4 poises at 70° F.

Method.—Heat 20% of oil and all the resin to 260° C. When clear, add remaining oil gradually, keeping at 260° C. Cool to 180° C., thin, and add driers.

Medium H (100% Phenolic-Resin/Linseed-Oil).

100% phenolic resin (Bakelite No. R.10840)	20.0
Varnish linseed-oil	40.0
Cobalt acetate	0.4
White spirit	39.35
Soligen lead cobalt	0.20
Soligen lead manganese	0.05

Sp. gr., 0.913 at 70° F. Viscosity, 5.6 poises at 70° F.

Method.—Heat varnish linseed-oil and resin to 293° C. in 45 min. and hold for approximately 1 hr. to a long string. Add cobalt acetate, cool, thin, and add driers in solution.

APPENDIX B.—*Experimental Data and Results.*

As in the case of the earlier series of tests, full details of all pertinent information have been recorded throughout the whole course of the experiments, including the formulation and manufacture of the paints, the preparation of the specimens by weathering prior to painting, the painting and exposure of the specimens, their inspection on the raft during immersion, and their final examination in the laboratory. These data will be kept in the Corrosion Committee's files and will be made available on request to anyone who is particularly interested in them. The authors have decided, after careful consideration, to present here the minimum essential of this mass of experimental evidence (Tables IX. and X.) to enable the reader to follow and appraise for himself the conclusions advanced in the text of this paper. They would further request any reader who may not be perfectly clear regarding some detailed point of experimental technique to be good enough to refer to their earlier paper* in which the testing procedure adopted is described at some length in the appendices.

The following explanatory note with regard to Table IX. may be helpful :

Columns (1) and (2).—The key to the code used in column (2) will be found in Fig. 1.

Columns (3)–(5).—The individual constituents of the pigment mixture are present in the proportions indicated by the code formulation. Thus, in the case of paint No. 149, *crx* 211/A, there are 50 parts of basic lead sulphate, 25 parts of zinc tetrahydroxy-chromate, and 25 parts of extender (Burntisland red and barytes mixed in equal proportions by weight) in 100 parts by weight of the pigment mixture. In the paint, as finally adjusted and applied to the test-specimens, these 100 parts of pigment were incorporated with 45

parts of medium A and 43 parts of thinners (naphtha). The formulations of this and of the other experimental media have already been given in Appendix A.

Columns (6) and (7).—These columns refer to the paints as finally adjusted. The efflux time relates to the time of flow in seconds of the first 50 c.c. of paint from a full No. 4 Ford cup at 70° F.

Column (8).—One-pint samples of all the paints were stored for periods of about 6 months, both at laboratory temperature and at 120° F. At the end of the test they were carefully examined for ease of re-mixing, brushability, and drying time. In addition, the efflux time (Ford cup) was re-determined; this led to some interesting observations, but it would be foreign to the end of this report to pursue them in detail. For the present purpose it will suffice to summarize the results of the storage tests as a whole in the three following categories: *G* good, *S* satisfactory, *X* needs improvement.

Columns (9)–(11).—The figures given in these columns are based on the weights of paint applied in each coat and represent mean values for each pair of specimens coated with the same paint. The data presented are :

I.—The spreading rate of the first coat of anti-corrosive paint in square yards per gallon.

II.—The total film thickness, *i.e.*, two coats of the anti-corrosive paint plus the finishing coat of anti-fouling paint AF10/43, in microns. These are calculated values based on the known non-volatile contents and specific gravities of the paints.

III.—The total weight of the dry paint film in grammes per specimen. These figures may be converted to ounces per square foot by multiplying by 0.016.

Column (12).—The merit figure is the general index of the performance of the paint and has been deduced as described in the main text. The general classification of the paints as regards protective properties is indicated thus: *V* very good, *G* good, *M* moderate, *B* bad.

Table X. contains more detailed data for eight typical paints, including one in each of the four classification groups, both in the case of paints of the basic lead sulphate or zinc oxide series and of paints of the graphite plus mineral black series. Results for the proprietary control are also included; it will be noted that this painting system gave an appreciably smaller film thickness than the experimental paints although, of course, it was applied under the same conditions.

It is hoped that the figures given in Table X. will convey some idea of the absolute performance

* F. Fancutt and J. C. Hudson, *Journal of The Iron and Steel Institute*, 1944, No. II., p. 269 P.

TABLE IX.—*Summary of Formulation, Physical Properties, and Test Results for Paints Nos. 149–275.*

Paint.		Composition of Paint.			Physical Properties.		Storage Properties.	Details of Application.			Merit Figure and Classification.	
		Parts by Weight per 100 Parts of Pigment.		Pigment/Non-Volatile Vehicle Ratio by Weight.	Specific Gravity.	Efflux Time, secs.		I.	II.	III.		
No.	Code.	Medium.	Naphtha.									
(1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	(9).	(10).	(11).	(12).	

A.—Basic Lead Sulphate Series.

(i) *Zinc tetrahydroxy-chromate.*

149	crx 211/A	45	43	3.49	1.62	44	S	68	133	60	9	M
150	crx 211/B	49	16	3.48	1.86	45	S	66	144	72	20	G
151	crx 211/C	56	35	3.49	1.56	20	S	92	112	51	9	M
152	crx 211/D	58	41	3.47	1.50	46	S	73	125	57	8	M
153	crx 241/A	54	61	2.85	1.44	46	S	84	120	52	2	B

(ii) *Barium chromate.*

154	cnx 211/A	39	24	4.0	1.70	42	S	63	154	73	18	G
155	cnx 211/B	43	11	3.97	1.95	45	S	63	158	79	25	V
156	cnx 211/C	50	19	3.97	1.74	37	S	73	128	61	10	M
157	cnx 211/D	51	30	3.95	1.66	46	S	65	129	64	9	M
158	cnx 241/A	42	38	3.73	1.64	45	S	81	129	60	8	M

(As No. 154 but with different pigment/vehicle ratios.)

232	cnx 211/A	20	34	7.94	2.02	48	S	79	112	68	1	B
233	cnx 211/A	29	32	5.3	1.80	33	S	80	129	64	5	B
234	cnx 211/A	49	41	3.18	1.60	46	S	66	135	63	9	M
235	cnx 211/A	59	45	2.65	1.52	47	S	57	143	64	15	G

(iii) *Zinc chromate.*

159	cqx 212/A	41	40	3.83	1.60	38	S	74	125	58	12	M
160	cqx 212/B	44	15	3.83	1.84	25	S	89	133	62	13	M
161	cqx 212/C	51	19	3.83	1.70	25	S	75	118	55	16	G
162	cqx 212/D	53	37	3.83	1.56	45	S	76	112	53	9	M
163	cqx 212/E	1.15	1.30	46	X	58	121	49	27	V
164	cqx 212/F	41	17	3.84	1.82	46	S	52	153	73	16	G
165	cqx 212/G	47	43	3.82	1.51	46	X	65	124	57	10	M
166	cqx 211/A	39	38	3.97	1.64	39	S	57	136	62	7	M
167	cqx 421/A	38	37	4.09	1.66	41	S	66	138	66	14	G
168	cqx 122/A	43	55	3.58	1.48	37	S	65	129	56	7	M
169	cqx 241/A	41	47	3.79	1.52	46	S	61	141	63	8	M

(As No. 168 but with extended milling times.)

272	cqx 122/A	43	53	3.58	1.49	40	S	60	133	60	3	B
273	cqx 122/A	43	53	3.58	1.49	44	S	59	130	59	7	M

(iv) *Red lead.*

170	cax 212/A	38	28	4.12	1.80	...	S	80	120	57	1	B
171	cax 211/A	35	25	4.40	1.88	41	S	52	162	81	16	G

(v) *White lead.*

172	cbx 214/A	40	38	3.85	1.65	46	S	80	119	55	9	M
173	cbx 212/A	38	35	4.09	1.74	41	S	63	134	68	17	G
174	cbx 212/B	41	11	4.10	2.02	43	S	71	151	82	28	V
175	cbx 212/C	48	17	4.10	1.81	35	S	80	119	58	7	M
176	cbx 212/D	49	31	4.11	1.64	40	S	79	114	56	5	B
177	cbx 212/E	1.15	1.28	56	X	57	125	50	26	V
178	cbx 212/F	38	15	4.09	1.90	46	S	71	146	70	16	G
179	cbx 212/G	44	34	4.10	1.65	43	S	71	118	57	11	M
180	cbx 211/A	35	33	4.37	1.80	33	S	71	129	62	14	G
181	cbx 421/A	34	31	4.59	1.89	43	S	71	132	72	17	G
182	cbx 210/A	32	23	4.90	2.05	43	S	52	146	81	20	G
183	cbx 122/A	38	29	4.04	1.76	46	S	65	149	72	16	G
184	cbx 241/A	33	25	4.63	1.94	46	S	64	150	81	19	G

274	cbx 212/H	40	12	4.095	1.90	46	S	63	163	80	(25)	(V)
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TABLE IX.—Continued.

Paint.		Composition of Paint.			Physical Properties.		Storage Properties.	Details of Application.			Merit Figure and Classification.	
		Parts by Weight per 100 Parts of Pigment.		Pigment/ Non-Volatile Vehicle Ratio by Weight.	Specific Gravity.	Efflux Time, secs.		I.	II.	III.		
No.	Code.	Medium.	Naphtha.									
(1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	(9).	(10).	(11).	(12).	
(vi) <i>Aluminium.</i>												
185	cgx 212/A	40	52	1.656	1.24	45	G	60	142	53	23	V
186	cgx 212/B	43	7	1.68	1.43	37	S	65	143	56	25	V
187	cgx 212/C	50	16	1.69	1.29	45	S	66	138	50	7	M
188	cgx 212/D	51	26	1.70	1.27	44	S	62	121	47	3	B
189	cgx 212/E	1.15	1.28	59	X	67	128	53	28	V
190	cgx 212/F	40	17	1.66	1.36	46	G	66	154	57	13	M
191	cgx 212/G	46	30	1.66	1.19	46	S	54	130	47	7	M
192	cgx 211/A	37	53	1.47	1.20	45	G	60	136	50	14	G
193	cgx 421/A	35	23	1.365	1.16	44	S	54	156	53	24	V
194	cgx 122/A	42	38	1.04	1.20	47	S	68	144	49	17	G
195	cgx 241/A	37	36	0.781	1.04	32	S	50	157	44	11	M
(vii) <i>Zinc.</i>												
196	cmx 201/A	52	38	4.40	1.66	45	S	65	165	70	21	G
197	cmx 211/B	38	9	4.42	2.20	40	S	75	143	78	24	V
198	cmx 211/C	44	12	4.42	1.98	42	S	65	137	73	13	M
199	cmx 211/D	46	20	4.41	1.82	44	S	70	117	56	5	B
200	cmx 122/A	37	31	4.23	1.78	27	X	72	138	67	10	M
B.—Zinc Oxide Series.												
(i) <i>Zinc tetrahydroxy-chromate.</i>												
201	jrx 211/A	49	69	3.16	1.42	59	S	75	117	52	1	B
202	jrx 211/B	53	30	3.16	1.60	64	S	71	126	57	1	B
203	jrx 211/C	62	50	3.15	1.45	63	S	77	111	51	5	B
204	jrx 211/D	61	71	3.33	1.36	62	S	67	113	52	3	B
205	jrx 241/A	57	74	2.75	1.36	61	S	73	124	53	2	B
(ii) <i>Barium chromate.</i>												
206	jnx 211/A	44	53	3.56	1.48	64	S	60	141	63	0	B
207	jnx 211/B	48	25	3.55	1.70	62	S	68	130	63	5	B
208	jnx 211/C	55	38	3.56	1.48	58	S	65	134	59	5	B
209	jnx 211/D	57	59	3.56	1.40	63	S	74	112	51	3	B
210	jnx 241/A	44	63	3.51	1.46	55	S	55	128	58	1	B
(iii) <i>Zinc chromate.</i>												
211	jqx 211/A	43	53	3.57	1.54	48	S	71	119	56	4	B
212	jqx 211/B	52	28	3.24	1.60	57	S	83	128	58	7	M
213	jqx 211/C	55	33	3.57	1.55	42	S	65	127	58	4	B
214	jqx 211/D	56	49	3.57	1.45	56	X	65	127	57	1	B
215	jqx 211/E	1.145	1.29	58	S	57	122	51	25	V
216	jqx 211/F	44	13	3.57	1.82	65	G	55	165	78	22	V
217	jqx 211/G	51	61	3.56	1.36	64	X	51	139	59	8	M
218	jqx 521/A	43	48	3.68	1.54	46	X	66	132	60	6	B
219	jqx 112/A	45	49	3.47	1.47	58	X	60	141	62	6	B
220	jqx 221/A	44	52	3.57	1.50	60	X	59	131	59	11	M
221	jqx 241/A	44	49	3.56	1.50	65	S	50	150	67	9	M
222	jqx 142/A	45	47	3.49	1.50	64	S	66	139	61	4	B
275	jqx 211/H	46	15	3.58	1.74	65	S	64	158	72	(6)	(B)
(iv) <i>Red lead 1, white lead 2.</i>												
223	jvx 211/A	40	47	3.88	1.60	66	S	59	129	62	3	B
224	jvx 241/A	36	37	4.33	1.80	58	S	59	123	65	0	B
(v) <i>White lead.</i>												
225	jbx 211/A	40	49	3.86	1.66	58	S	79	113	58	0	B
226	jbx 241/A	36	39	4.32	1.78	64	S	79	119	62	1	B

TABLE IX.—Continued.

Paint.		Composition of Paint.			Physical Properties.		Storage Properties.	Details of Application.			Merit Figure and Classification.	
		Parts by Weight per 100 Parts of Pigment.		Pigment/ Non-Volatile Vehicle Ratio by Weight.	Specific Gravity.	Efflux Time, secs.		I.	II.	III.		
No.	Code.	Medium.	Naphtha.									
(1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	(9).	(10).	(11).	(12).	
(vi) <i>Aluminium.</i>												
227	<i>jgx 211/A</i>	43	43	1.41	1.14	43	<i>G</i>	54	135	48	4	<i>B</i>
228	<i>jgx 211/B</i>	47	22	1.41	1.35	31	<i>X</i>	81	126	49	10	<i>M</i>
229	<i>jgx 211/C</i>	55	39	1.40	1.51	44	<i>S</i>	73	96	48	6	<i>B</i>
230	<i>jgx 211/D</i>	56	49	1.41	1.15	42	<i>X</i>	55	121	46	0	<i>B</i>
(vii) <i>Zinc.</i>												
231	<i>jmx 211/A</i>	40	48	3.91	1.62	61	<i>X</i>	83	115	55	3	<i>B</i>
C.— <i>Graphite and Mineral Black Series.</i>												
(i) <i>Zinc tetrahydroxy-chromate.</i>												
236	<i>frk 110/A</i>	62	59	2.50	1.34	92	<i>X</i>	79	137	55	8	<i>M</i>
237	<i>frk 231/A</i>	61	69	2.53	1.28	82	<i>X</i>	80	126	47	3	<i>B</i>
238	<i>frk 132/A</i>	61	40	2.54	1.30	88	<i>X</i>	67	167	56	2	<i>B</i>
239	<i>frk 011/A</i>	61	64	2.54	1.29	86	<i>X</i>	47	156	59	6	<i>B</i>
(ii) <i>Barium chromate.</i>												
240	<i>fnk 211/A</i>	54	19	2.89	1.45	70	<i>G</i>	64	168	62	9	<i>M</i>
241	<i>fnk 432/A</i>	53	24	2.94	1.49	80	<i>G</i>	57	164	64	7	<i>B</i>
242	<i>fnk 221/A</i>	52	28	2.98	1.48	82	<i>G</i>	58	157	63	6	<i>B</i>
243	<i>fnk 110/A</i>	52	20	2.98	1.58	78	<i>G</i>	56	166	68	13	<i>M</i>
244	<i>fnk 231/A</i>	51	18	3.05	1.58	79	<i>G</i>	74	172	70	15	<i>G</i>
245	<i>fnk 132/A</i>	50	23	3.07	1.56	91	<i>S</i>	66	161	67	4	<i>B</i>
246	<i>fnk 011/A</i>	50	26	3.09	1.50	80	<i>S</i>	78	143	56	5	<i>B</i>
247	<i>fnk 241/A</i>	50	25	3.11	1.56	40	<i>G</i>	70	146	61	3	<i>B</i>
(iii) <i>Zinc chromate.</i>												
248	<i>fqk 211/A</i>	53	22	2.91	1.44	98	<i>X</i>	55	180	63	15	<i>G</i>
249	<i>fqk 432/A</i>	52	39	2.97	1.36	91	<i>X</i>	52	168	63	13	<i>M</i>
250	<i>fqk 221/A</i>	52	40	3.07	1.38	82	<i>X</i>	64	155	60	8	<i>M</i>
251	<i>fqk 110/A</i>	51	33	3.075	1.42	81	<i>X</i>	69	161	62	18	<i>G</i>
252	<i>fqk 231/A</i>	50	35	3.09	1.38	72	<i>X</i>	56	164	62	8	<i>M</i>
253	<i>fqk 132/A</i>	50	37	3.09	1.40	84	<i>X</i>	56	170	63	15	<i>G</i>
254	<i>fqk 011/A</i>	50	41	3.10	1.38	92	<i>X</i>	60	165	63	18	<i>G</i>
255	<i>fqk 241/A</i>	49	30	3.14	1.43	84	<i>X</i>	67	160	61	9	<i>M</i>
(iv) <i>Red lead 1, white lead 2.</i>												
256	<i>fvk 211/A</i>	50	33	3.10	1.48	82	<i>G</i>	66	149	61	6	<i>B</i>
257	<i>fvk 432/A</i>	48	27	3.24	1.52	56	<i>S</i>	79	148	60	8	<i>M</i>
258	<i>fvk 221/A</i>	46	21	3.36	1.70	80	<i>S</i>	56	167	73	10	<i>M</i>
259	<i>fvk 110/A</i>	44	19	3.56	1.80	75	<i>S</i>	63	154	71	4	<i>B</i>
260	<i>fvk 231/A</i>	43	22	3.58	1.68	48	<i>S</i>	63	155	67	6	<i>B</i>
261	<i>fvk 132/A</i>	43	21	3.60	1.66	58	<i>S</i>	73	149	65	3	<i>B</i>
262	<i>fvk 011/A</i>	43	19	3.61	1.68	70	<i>S</i>	67	158	67	7	<i>B</i>
263	<i>fvk 241/A</i>	42	18	3.75	1.75	60	<i>S</i>	61	155	70	8	<i>M</i>
(v) <i>Basic lead sulphate.</i>												
264	<i>fck 211/A</i>	51	33	3.06	1.45	86	<i>G</i>	60	173	69	17	<i>G</i>
265	<i>fck 432/A</i>	48	33	3.245	1.49	90	<i>G</i>	51	169	69	23	<i>V</i>
266	<i>fck 221/A</i>	46	33	3.415	1.52	86	<i>G</i>	51	158	67	17	<i>G</i>
267	<i>fck 110/A</i>	44	30	3.56	1.59	81	<i>S</i>	56	154	68	22	<i>V</i>
268	<i>fck 231/A</i>	43	31	3.56	1.59	88	<i>S</i>	62	147	65	13	<i>M</i>
269	<i>fck 132/A</i>	43	33	3.60	1.58	73	<i>S</i>	71	145	64	19	<i>V</i>
270	<i>fck 011/A</i>	43	37	3.62	1.52	55	<i>S</i>	77	135	58	6	<i>B</i>
271	<i>fck 241/A</i>	41	30	3.75	1.62	75	<i>S</i>	52	166	73	19	<i>V</i>

TABLE X.—*Typical Experimental Results.**

	Basic Lead Sulphate or Zinc Oxide Series.				Proprietary Control.	Graphite and Mineral Black Series.			
	Very Good.	Good.	Moderate.	Bad.		Very Good.	Good.	Moderate.	Bad.
Merit Figure.	25.	16.	9.	3.	—.	22.	17.	9.	5.
Paint. { No. Code.	186.	178.	172.	223.	—.	267.	264.	255.	246.
	<i>cgx</i> 212/B.	<i>cbx</i> 212/F.	<i>cbx</i> 214/A.	<i>jvx</i> 211/A.		<i>fck</i> 110/A.	<i>fck</i> 211/A.	<i>fgk</i> 241/A.	<i>fnk</i> 011/A.
<i>Details of Coating Weight, &c.</i>									
Spreading rate of first coat of paint, sq. yd./gal. :									
I	62	73	82	64	131	58	67	69	82
II	68	68	78	55	125	54	54	65	75
Total paint film thickness, μ :									
I	141	135	117	123	...	150	159	169	142
II	145	157	122	134	...	157	188	151	145
Total weight of dry paint, g. :									
I	54	67	53	59	29	66	64	64	55
II	58	73	56	66	32	70	75	57	57
<i>Results of Field Inspections.</i>									
Total index figure :									
I	133	279	645	480	423	95	154	171	377
II	340	287	330	335	558	468	398	566	407
Index figure (rusting only) :									
I	12	50	226	196	225	6	13	22	90
II	10	16	14	14	111	7	17	174	9
<i>Results of Laboratory Examination.</i>									
Intact paint, % :									
I	97	93	90	54	29	94	88	92	17
II	100	96	96	85	75	96	97	89	65
Rusting, % :									
I	1.0	2.5	4.8	8.3	19.2	1.2	2.3	3.8	7.3
II	Nil	1.3	1.1	2.3	21.3	1.7	1.6	7.7	1.7
Loss in weight, g. :									
I	3	5	9	41	18	9	9	11	33
II	1	5	7	9	4	3	3	10	26
<i>Results of Storage Tests.†</i>									
At 70° F.; 8 months .	<i>S</i>	<i>S</i>	<i>S</i>	<i>S</i>	...	<i>S</i>	<i>S</i>	<i>Xf</i>	<i>S</i>
At 120° F.; 6 months .	<i>p</i>	<i>Xs</i>	<i>p</i>	<i>Xs</i>	...	<i>Xs</i>	<i>S</i>	<i>Xg</i>	<i>p</i>

* An explanation of the data presented is given in the text.

† *S*, satisfactory; *X*, needs improvement; *f*, excessive fattening; *g*, gelled; *p*, gas pressure developed; and *s*, hard settlement.

of the painting schemes and of the significance of the merit figures. They certainly illustrate the fact that the various methods of assessing the test results are not entirely consistent and that no single one of them is an infallible criterion of relative merit. On the other hand, as already

described, the final merit figure represents the sum total of assessments for five different properties made on duplicate specimens; as such, it may be regarded as a reasonably accurate indication of the protective values of the paint concerned.

REPORT ON ANTI-FOULING RESEARCH, 1942-44.*

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Paper No. 20/1946 of the Corrosion Committee (submitted by the Marine Corrosion Sub-Committee†).

(Fig. 4 = Plate XLIII.)

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SYNOPSIS.

The technique of exposure tests on anti-fouling compositions is described. Patch tests of a minimum area (12×8 in.) on a larger panel are employed for comparative work. The test patches are arranged at random to eliminate systematic errors. "Seasoned" panels painted with the best possible protective system are used.

The assessment of fouling on the panels is carried out by examination in a sea-water tank, emphasis being laid on the kinds of organism present rather than on the quantity. Suitable dates for commencing tests are in spring for short-period tests and in autumn for long-period tests.

The sequence of settlement of fouling organisms is not a causal chain but is largely determined by the seasonal occurrence of the settling stages of each organism. Sequences may, however, develop on a toxic surface owing to gradual decrease in toxicity.

Emphasis is laid on the importance of qualitative fouling assessments which determine the time of breakdown of the anti-fouling protection; quantitative measures, though valuable for some purposes, are used more as indicators of external factors in the environment.

The seasonal settlement of fouling forms at Millport is described briefly, and is compared with conditions elsewhere in the British Isles.

The susceptibility of fouling organisms to poisons varies considerably and can be employed to determine grades of anti-fouling efficacy.

The part played by bacterial slime in fouling is discussed at some length. It is not a necessary precursor of fouling, but is highly resistant and readily developed on rosin-containing coatings. It therefore

* Received January 28, 1946. This paper is published by authority of the Corrosion Committee. The views expressed in it are the author's, and are not necessarily endorsed by the Committee as a body.

† A Sub-Committee of the Joint Corrosion Committee of The Iron and Steel Institute and the British Iron and Steel Federation reporting to the Iron and Steel Research Council.

tends to develop early and may influence subsequent settlements to a limited extent. This slime does not serve as a cumulative store of poison over a toxic paint.

The principal features of diatom, seaweed, and animal fouling organisms are described, particular attention being paid to such factors as season of occurrence, mode of settlement and attachment, and relative susceptibility to poisons.

A brief analysis of the factors concerned in the fouling on ships' bottoms is accompanied by a summary of the results of a preliminary study of samples from 30 voyages to tropical waters.

The mode of action of anti-fouling coatings is demonstrated by an experiment giving a toxic border around a patch of anti-fouling composition. The toxicity appears to be produced by a thin layer of poisonous sea-water immediately over the paint surface.

The loss of poison from the paint into this toxic layer is correlated with chemical analysis of the copper and mercury content of sea-water in which painted panels are immersed; this process is known as the leaching test. Under the experimental conditions prescribed, a rate of loss of copper of 10 $\mu\text{g./sq. cm./day}$ in the laboratory test is an adequate indicator of successful anti-fouling properties. In the presence of mercury this rate of loss of copper may be lower.

The leaching technique is described and suitable methods for the estimation of copper and mercury in the leachate are presented.

Preliminary studies of the effect on the laboratory leaching rate of varying the paint constituents are given. The most important factor is the resin component. In a rosin-linseed-oil varnish, replacement of the rosin by ester gum, acid or neutral synthetic resins, waxes, lanolin, bitumen or (by decreasing the rosin content) drying oil, all produce a fall in the copper leaching rate, which in a rosin-oil varnish is approximately proportional to the copper content of the paint film. Mercuric oxide also lowers the copper leaching rate from a cuprous oxide paint.

The practical significance of this leaching test is at present limited to the prediction of success or failure of the anti-fouling properties of a formulation. It has only a very limited value in estimating the effective anti-fouling life, since the leaching slides are stored in laboratory tanks and lose poison less rapidly than in the sea. Methods of overcoming this difficulty are being explored and the existing technique is a useful laboratory tool in working out practical paint formulations.

Experiments on the use of organic poisons in anti-fouling compositions are described. Certain organic arsenicals, a number of organic sulphur compounds, and organomercurial derivatives offer possibilities of development, but a large number of highly toxic compounds fail as anti-fouling agents. This failure is very largely correlated with high solubility in the non-polar solvents.

A description of a promising development in an aqueous cementiferous composition using organic poisons as anti-fouling agents is given. Compositions of this type open up the possibility of applying a single-coat system, firmly adherent to wet, rusty, or mill-scale-covered steel, which is adequate for anti-corrosive and anti-fouling purposes, and which may be dried out after long periods of immersion without any deleterious effect.

Introduction.

The present report is an endeavour to collect together the salient features of the anti-fouling work of the Marine Corrosion Sub-Committee up to 1944, when the author resigned his appointment as Investigator to the Sub-Committee. The work has very greatly expanded since the completion of the First Report,* and it is impossible to make this account exhaustive. In an attempt to piece together the different lines of attack into a single coherent whole, one is bound to sacrifice much experimental material which is detailed or only remotely related to the main outline. It will be useful to consider the work under roughly the same headings as in the former report, and to distinguish between the biological approach to the problems of fouling and the (largely) chemical approach to the anti-fouling problem. It is perhaps unnecessary to point out that these are two different angles from which the same problem is being

studied and, in consequence, there is considerable overlapping between the sections.

From the point of view of continuity it has been thought best for the present account to be written by a single author, although the work has been the product of a team of investigators. To some extent, different fields of experiment were allocated to individual investigators but this was rarely, if ever, completely possible. Thus, much of the work on slime and its rôle in fouling was done by Dr. M. F. Spooner; the seasonal occurrence and settlement mechanisms of barnacles were dealt with by Mr. K. A. Pyefinch; work on organic poisons in anti-fouling paints was divided between Dr. H. Barnes and Miss F. A. Stanbury at Plymouth, who also carried out the laboratory investigations, and the Millport team, who planned the exposure tests. The leaching tests, which form the basis of much of this report, were started with methods developed by the author in 1941 and have now expanded so greatly in scope as to employ

* First Report of the Marine Corrosion Sub-Committee, *Journal of The Iron and Steel Institute*, 1943, No. I., p. 339 P.

the Millport team for a very large amount of its time.

A very high proportion of members of the Sub-Committee have given much of their time and that of their staffs to various special problems. Whenever practicable, mention is made in the text of the various persons mainly responsible for a particular development, but the whole project has been from first to last an essay in team-work.

It is hoped that in the near future the contribution which individual workers have made will be followed by the production of a series of more specialized papers (some of which, by reason of

The raft consists essentially of four longitudinal timbers (9 in. \times 9 in. \times 23 ft.), on which are bolted eight transverse timbers (9 in. \times 9 in. \times 16 ft.). Each transverse timber is lapped at the ends and notched 3 ft. from the end to rest on the longitudinals, so that the whole framework appears in dissected isometric view as in Fig. 1. One-inch planking forms a catwalk over the longitudinal timbers on both sides and stanchions with an iron-pipe railing run the whole length of both catwalks.

Buoyancy is maintained by the very simple means of a row of empty 40-gal. drums pushed under the sides until they come to rest wedged

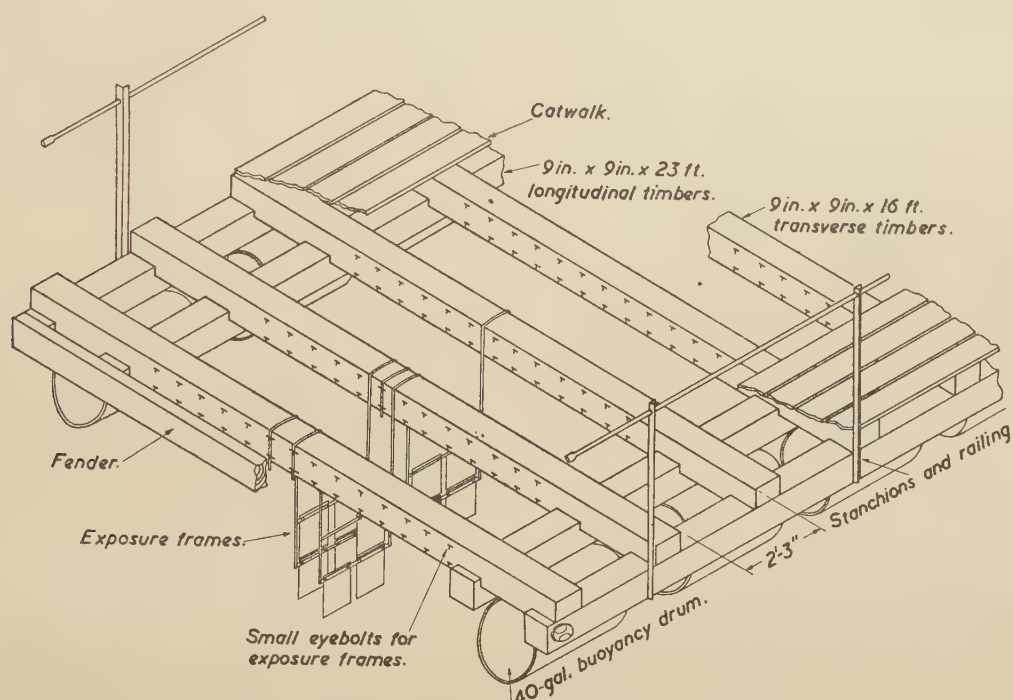


FIG. 1.—Dissected Isometric View of Half the Large Millport Exposure Raft.

their scope and subject, may be more suited to the pages of a biological or chemical journal) under the name of the individual who has been principally responsible for the detailed field in question.

I.—Technique of Exposure Tests.

The Sub-Committee maintains three testing rafts at the Marine Station at Millport. The smallest of these is 9 \times 6 ft. and accommodates 20 exposure frames; the second is 12 \times 10 ft. and takes 60 frames, and the main raft, which not only accommodates 95 frames, but also has more working space for the investigators, is 23 \times 16 ft. All the rafts are of very simple construction and the largest is perhaps worth describing in greater detail.*

between the two longitudinal beams (see Fig. 1). In calm weather two or three men can "tread-mill" a drum down until it is pulled into position under the beams by one or two more men on the opposite side of the raft. The drum is firmly held in place by its own buoyancy; no ropes are needed to secure it, and if it leaks, it ultimately fills and falls away, leaving a gap which is easily seen and can be filled by introducing another drum at any time. The raft will accommodate seven of these drums on each side, giving a total lift of some 5000 lb. in addition to that provided by the wooden longitudinal beams. (The transverse beams are practically out of water—a necessity for comfortable working.)

Specimens are hung from mild-steel hooks ($\frac{3}{8}$ or $\frac{1}{2}$ in. dia. in cross-section) slung over the

* This raft was built through a special grant generously provided by the Shipbuilding Conference.

transverse timbers. The space between two adjacent transverse beams will just accommodate a plate 24 in. wide, which is hung on two such hooks so that its plane lies along the length of the raft. Smaller specimens are bolted on frames such as those seen in Fig. 1, which accommodate four plates 15 × 10 in., or eight plates 6 × 5 in., in two rows. The upper edge of single plates and of the top row of plates in a frame is approximately 18 in. below the water level; this distance varies slightly with the loading on the raft.

The hooks are inserted into eyebolts bolted on to the sides of the transverse timber; since the beams are only 2 ft. 3 in. apart, one person standing astride the bay can readily remove and replace a specimen or frame.

Specimens are usually insulated from the hangers and from the bolts by fibre sleeves and washers identical to those used in the Sub-Committee's corrosion tests at Caernarvon. The steel plates are treated in various ways before exposure, the most usual technique involving pickling and "seasoning." After pickling in cold 5% hydrochloric acid, the plate is washed and scrubbed down in hot water, left to dry thoroughly, and after seven days is given a single coat of anti-corrosive. It is immersed on the raft for at least a month in this condition, after which it is brought in, washed and scrubbed with fresh water, and allowed to dry thoroughly for several days. The final anti-corrosive treatment involves two, or sometimes three, coats of a good protective composition (paint No. 173* of the Sub-Committee's anti-corrosive formulations has been used recently for this purpose). Each protective coat is given at least 24 hr. in which to dry.

The painting scheme for the experimental anti-fouling coatings varies with the type of experiment. In the comparison of large numbers of formulations in which one component of the paint system is varied, while the others are left constant, patch painting is much to be preferred. Visual comparison of adjacent test patches on the same panel provides a very reliable estimate of differences in fouling intensity; it is the standard practice to assess all such panels without reference to the key plan of the paints used and to correlate the fouling observations with the paints only on returning to the laboratory; this largely eliminates subjective factors in comparing paints.

A 24 × 24-in. panel is usually divided into twelve patches (six on each side). The patches are 12 × 8 in. in area, the 12-in. dimension being horizontal, so that the six test areas are arranged in two vertical columns and three horizontal rows. Patches are always painted in duplicate and often in triplicate; each panel exposed usually has a non-toxic patch (generally provided simply by omitting the final coating). The

patches—both anti-fouling and non-toxic—are so arranged that duplicate test surfaces are exposed, one being on the front of a panel and the other on the back; allowance is made in this way for variation in fouling due to differing light intensities on opposite sides of the panel. Subject to this primary grouping of test patches, the final arrangement is artificially randomized with the help of a table of "random sampling numbers."

It will be demonstrated later in this report that the "border effect" of a highly toxic patch of anti-fouling paint may poison organisms for a distance of several inches beyond the boundary of the patch. This phenomenon is commonly encountered at Millport, where the tidal current is very marked and curiously asymmetrical, the flood current being slower and less clearly defined than the rapid and steady ebb current. Such "border effects" rarely extend more than 3-4 in. on the "ebb" side of a toxic patch, and the 12-in. extension of each patch therefore serves to demonstrate the limits of such secondary anti-fouling action quite adequately.

For other experiments single plates of varying sizes and painted with only one type of anti-fouling have been used. This is particularly useful in dealing with long-lived compositions where it is annoying to retain a large patch-painted panel for the sake of one good area on it; for example, one small 6 × 5-in. specimen has now survived 39 months without fouling (though this is exceptional).

Other treatments of the steel basis are occasionally used; as-rolled, pickled, sand-blasted, and weathered plates are employed for special tests. But for testing the performance of formulated anti-fouling coatings, the view has been taken that it is reasonable to provide the anti-fouling composition with as perfect a paint substratum as it is possible to produce; it is only in this manner that accurate comparison of the anti-fouling properties can be made without introducing unpredictable variations due to corrosion troubles.

On all panels the weight of the anti-fouling composition applied to each patch (or to the single panel) is recorded. For a paint of reasonable consistency, application is at the rate of 0.5-0.6 oz./sq. ft.; but this factor varies with the consistency of the paint used.

For paints containing compounds of copper, mercury, phenyl mercury, or phenarsazine, it is standard practice to paint a number of ground-glass slides, 3 × 1 in., with a proportionate paint weight at the same time that the exposure panels are painted. These ground-glass slides are used for the leaching tests which are described later.

Panels are assessed at monthly intervals. In addition, an inspection is made at the end of the first two weeks and at other times if it appears

* For particulars of this paint and of the Sub-Committee's most recent work on anti-corrosive compositions see F. Fancutt and J. C. Hudson, *Journal of The Iron and Steel Institute*, 1946, No. II., p. 273 P (*this volume*).

necessary. For certain purposes "dry" assessments are made; the plate is merely removed from the sea and hung on a trestle for examination. For more detailed and accurate assessment of the fouling, most specimens are now examined when immersed in a shallow wooden tank of sea-water; by this means a trained observer can not only record the *species* of such large and obvious forms as adult barnacles and tubeworms, but can also recognize smaller organisms (*e.g.*, barnacle cyprids and settling stages of *Tubularia*) and the characteristic growth forms of microscopic diatoms and seaweeds. It would be difficult to exaggerate the usefulness of this method of studying fouled plates, which is very strongly recommended whenever it is possible. It also presents a decided advantage in that the specimen is kept in sea-water throughout the whole period of examination which can therefore be indefinitely prolonged without harmful consequences.

The period during which extensive fouling settlement may be encountered in British waters extends from April to September, inclusive. It follows that tests on long-service paints are best commenced in the late summer or autumn since this makes possible an accurate estimate of their period of protection between the limits of, say, 7-13 months. For paints whose anti-fouling properties are completely unknown, it is advisable to commence the exposures in the period March-June so that their ability to prevent settlement of fouling organisms during the first few months of their life can be accurately assessed. A poor paint immersed in October or November may often show a negligible settlement of fouling until the following April and thus give a completely fictitious length of life.

The three rafts at Millport differ in their situation and in their moorings. The large raft is moored to Keppel Pier at the south-west end, and with 30 fathoms of cable to a 300-lb. mushroom at the north-east end. The second raft is moored in a more open position in Balloch Bay and, being anchored only at one end, is free to swing with the tide. The smallest raft is temporarily moored a few yards out from the boat-slip at Keppel and is used for miscellaneous experiments (*e.g.*, electrical protection experiments) which might interfere with other tests on the two larger rafts. The frame design of the two smaller rafts is even simpler than that of the large one; they have neither catwalk nor railings and can only be used in reasonably calm weather.

The Keppel raft, as the asymmetry of its tidal current suggests, is situated in a bay just north of a small point such that the flood-tide produces an eddy current, while the ebb-tide runs much more uniformly. This eddy may be responsible for the occasional very intense fouling by certain organisms, *e.g.*, *Balanus balanoides* in 1944, when plates simultaneously exposed on the more open

Balloch raft showed no such dense settlement. The Keppel site is also adjacent to a very heavy source of algal and hydroid fouling and thus provides a very severe test for panels exposed there.

II.—The Biological Approach to the Problem of Fouling.

The general characteristics of the fouling growths in their early and later stages were described in the earlier report, and in this section the main headings will be used in the same sense as before.

(1) SEQUENCE OF SETTLEMENT OF FOULING ORGANISMS.

One point, which may be emphasized as summarizing the general trend of the biological work since the First Report, is the importance attached to what might be termed the fortuitous nature of fouling, particularly in relation to the sequence of fouling organisms encountered. It seems largely true to say that the sequence of settlement and growth upon a plate—especially if it is not painted with a poisonous coating—is almost entirely a function of the chronological order in which potential fouling organisms appear in the sea and of the rate at which they grow. There is no evidence yet of a causal sequence in the early stages of fouling. "Biological exclusion" (a portmanteau word which embraces a whole range of different types of interaction among a growing colony of organisms) coupled with the very widely differing rates of growth of organisms, frequently produces an apparent sequence of colonization which is causal only in its development and not in its settlement; the struggle for existence is not less severe in anchored forms than in mobile organisms, although the nature of the competition may be more subtle. Forests of living vegetation at and near the water-line, equally coated with extraneous deposits of mud and silt, seriously impede the feeding mechanisms of animals like the barnacle and tubeworm. The thick layers of rapidly growing bacterial slime developed during certain periods in relatively still water may strip off completely for mechanical reasons, carrying away with them a host of more complex forms anchored only insecurely in this biological quicksand. On the new substratum a fresh crop of types can settle more securely, and what at first sight appears to be the "causal" sequence slime \rightarrow organism $A \rightarrow$ organism B resolves itself into the complex determined by (1) the rapid growth of slime under fortuitously favourable conditions, (2) the presence of organism A at the correct stage of development to settle on the slime growth, and (3) the stripping of the slime with its attendant organism A , followed by a new colonization of the surface with the opportune arrival of organism B .

On a *poisonous* surface the sequence of settle-

ment may be determined by the ageing of the surface accompanied by its gradual decrease in toxicity. On such a surface the least sensitive organisms appear first and are followed later, if the environmental conditions are favourable, by other more sensitive forms. Bacterial slimes appear very resistant to poisons leached out from a painted surface; certain diatoms, including mucus-secreting forms, are less so; and the larger attached plants and animals are less resistant still. On many anti-fouling paint surfaces, therefore, these three types of growths will occur in a definite sequence, though even here the actual species present at any particular stage will vary with the season, the locality, and the many other factors which make for the temporary abundance or scarcity of each particular form at any one period.

It can thus be seen that a clear picture of the seasonal occurrence of fouling organisms is an all-important requirement in interpreting the growth on a fouled surface; coupled with a knowledge of the relative sensitivity to poisons of the different organisms, it enables the biologist to estimate the anti-fouling properties of a surface at a stage when the development of clearly visible fouling growths has not yet been reached. From the practical point of view it may be possible to say that an anti-fouling composition is unsatisfactory within a few days of immersion—or that a composition which later possesses satisfactory anti-fouling qualities has an initial stage during which it is highly susceptible to fouling.

That this latter point is not a purely academic one is shown by a test on a proprietary anti-fouling paint at Millport. In most of the tests carried out with plates immersed in the early part of the year (January–March) this paint proved successful in resisting fouling for long periods. A chemical test of its rate of loss of poison suggested that there was a short initial stage of low toxicity. This was confirmed by the immersion of a freshly coated panel in August, when a heavy settlement of the hydroid *Tubularia* was in progress. Within five days the plate was fouled with a fairly heavy growth of the hydroid which it retained (the hydroids increasing to their normal maximum size) throughout the whole winter.

A similar painted panel immersed in spring showed a heavy slime growth thickly populated with diatoms, sporelings, and filaments of seaweeds in the early stages. By the time sloughing of the slime took place, removing most of these secondary settlers, the toxicity had risen sufficiently to prevent further settlement.

As a matter of interest it may be added that this feature of the coating was found to be associated with a short drying time before immersion. A drying time of 6 hr. was allowed which under normal circumstances is ample for any anti-fouling composition, since many manufacturers recommend as little as 2 hr., which often obtains under practical conditions. When the time between painting and immersion of this anti-fouling coating was raised to 24 hr. the initial toxicity was found to be high enough to prevent fouling; with drying times less than 6 hr. the initial "fouling" period might be extended still further.

* These observations at Plymouth have been carried out by Dr. H. Barnes and Miss F. A. Stanbury.

(2) SEASONAL SETTLEMENT OF FOULING ORGANISMS.

The seasonal nature of fouling on a painted panel has been studied at Millport, Caernarvon, and Plymouth, by the immersion at regular intervals of 6 × 5-in. test panels. Each plate is removed at the end of intervals of 3–4 weeks and examined visually and microscopically to determine the species present. Longer-period exposure tests commencing at various times of the year have been examined from Plymouth* and Millport. Dr. M. F. Spooner and Miss J. C. Mott have been largely responsible for the observations recorded below.

In 1943, the Millport series showed a general picture which can be summarized as follows:

March.—Fouling almost entirely by diatom slime and filaments. Very few of the seaweed fouling organisms occur and much of the diatom is "floating" material and not the attached type.

April.—The "floating" diatom outburst is dying down and attached diatom filaments and slimes predominate.

May.—The attached diatoms reach their maximum. The few *Ectocarpus* and *Ulothrix* previously occurring are now reinforced by other species of seaweeds in appreciable numbers, e.g., *Cladophora* and *Enteromorpha* begin to appear.

June.—Hydroid fouling begins to be appreciable although the predominant fouling form is still of a seaweed type. *Obelia* is the dominant hydroid, with *Tubularia* occurring only in small numbers.

July.—The height of the plant fouling season, although the onset of the hydroid *Tubularia* is now evident. Calcareous tubeworms settle in considerable numbers.

August.—Plant fouling is now appreciably less, relatively few diatoms are found, and *Tubularia* is the dominant form. The calcareous tubeworm *Pomatoceros* is at its maximum; a type of sea-slug *Eolis* appears in considerable numbers and feeds on the heads of *Tubularia*.

September.—*Tubularia*, though still settling in considerable numbers, grows less strongly than before. Mussels are now beginning to appear in larger numbers, frequently anchoring themselves at the bases of tufts of *Tubularia*. *Pomatoceros* has almost disappeared.

October and November.—*Tubularia* is still present but only small colonies are found, the rate of growth now probably being restricted by the lower water temperature and the less abundant food supply. Mussels tend to predominate.

December.—Mussels and a very few *Tubularia* are in evidence.

January and February (1944).—Apart from an odd mussel or two, practically nothing settles on the plates during these months.

The absence of appreciable numbers of barnacles from the test-plates was one of the striking features of the 1943 fouling at Millport. This, however, must be regarded as a local anomaly as Caernarvon produced a very heavy barnacle settlement during April 1943. This settlement started in March and tailed off in May, June, July, and August (the later settlements were a different barnacle species), but the numbers settling in April were larger than those for all the rest of the year put together. During April 1944, Millport experienced a tremendously heavy settlement of barnacles and it lasted for about 3-4 weeks.

There is some reason to believe that the fouling on a panel as small as 6×5 in. is not completely representative of the total fouling which may appear on a larger surface. Recent tests have suggested the advisability of using panels 1-2 ft. sq., but the difficulties of transporting plates of this size to the many different field stations around Britain have made it necessary to depend largely on the smaller specimens for such comparative tests.

The Caernarvon-"season" begins earlier and continues appreciably longer than that at Millport. Considerable algal fouling at Caernarvon was recorded from March to November inclusive, the greatest settlement being during July and August. *Tubularia* never attained the density recorded at Millport, though at both sites this hydroid was at its height during August. It did not occur after September at the Caernarvon site.

At Plymouth the season is long, as at Caernarvon, and the peak of many organisms occurs still earlier in the year. Algal fouling was highest in May-June, and *Tubularia* in July. Neither at Plymouth nor at Caernarvon were mussels encountered to a similar extent to that at Millport. No barnacles settled at the raft site at Plymouth.

The results above are all based on plates exposed for not more than one month. The fouling on a plate which has been immersed for some time presents a picture in which the simple seasonal settlement may become greatly obscured by exclusion and growth-rate effects. Thus, plates immersed by Miss F. A. Stanbury on April 10, 1942, at Plymouth, showed in August an almost continuous mat of the colonial sea-squirt *Diplosoma*, which prevented the settlement of all other forms until September, when its death and decomposition by fungal growth left free space which was colonized by newly settled mussels.

In a similar manner, plates exposed in the late summer at Millport foul with mussels in the autumn and develop a solid growth of these to the exclusion of almost all other forms; during the winter the mussels grow to such an extent that they and their thread-like attachments to the plate completely prevent further colonization of the surface.

Barnacles show similar characteristics if a heavy settlement of them becomes well established. Solid colonies of tall laterally compressed forms have at times covered every available square millimetre of the plates at Caernarvon; no other growth can develop except on the barnacle shells themselves.

The above account suggests that, on a non-poisonous plate, the fouling on the plate at any period is likely to depend much more on its early history soon after immersion than on the forms present in the sea at the time of inspection; the latter may indeed often be conspicuous only by their absence. Sequences of organisms on a plate are principally determined by similar causes; if the plate is only sparsely colonized, or if the previous colonizers are dying off, many forms present in the settling stages will successfully invade the plate.

(3) SUSCEPTIBILITY OF ORGANISMS TO POISONS.

On a poisonous plate further factors must be considered. The numerous types of organisms capable of fouling a plate have very different degrees of susceptibility to the poisons used; selective colonization can therefore occur at a time when the composition is commencing to fail, and a form which in open biological competition on a non-poisonous surface cannot hold its own with contemporary invaders may become almost the sole occupant.

Several diatom species are well qualified to occupy this position. *Achnanthes*, *Schizonema*, and *Amphiprora* at Millport can become established as long-lasting grey or brown slimes and filaments on plates which, if they were completely non-toxic, would show these invaders as only a passing phase or which would be almost completely absent from the fouling. Once well established, such diatom films may discourage the invasion of newcomers by coating the whole surface with their slimy growths and by affording a very unfavourable substratum for (particularly) certain types of animals. One composition tested shows this feature extremely well; if put out in a season of heavy barnacle settlement it may collect very large numbers of these organisms; but if immersed earlier it may become so completely coated with the diatom *Achnanthes* that a later barnacle settlement scarcely affects it. Such a paint applied to a vessel may well give a fictitious anti-fouling value.

It is highly probable that many paints which behave with moderate success in temperate waters (where, with few exceptions, fouling develops on the whole rather slowly and competing forms all get some chance of settling) may fail catastrophically to prevent a settlement of barnacles in tropical waters, if this settlement occurs very soon after the ship puts into port. A

heavy diatom or bacterial slime grown in the first few weeks in a temperate port will collect few additional animal forms; when the ship puts to sea the slime washes off and the vessel is clean. The same vessel visiting a tropical port at a period of heavy barnacle or tubeworm settlement will within a few days become completely covered with these organisms.

(4) THE ASSESSMENT OF FOULING IN EXPOSURE TESTS.

The above introduction to the biological problems of fouling, though somewhat lengthy, may serve to illustrate the importance of a correct basis for assessing the failure by fouling of an exposed plate.

It has already been suggested (*see the discussion on the First Report, loc. cit.*, p. 447 P) that raft tests form a very severe basis on which to judge an anti-fouling composition. Panels submerged at such a site are almost continuously exposed to infection by a large variety of animal and plant species which may vary widely in their resistance to poisoning. In the absence of rapid water flow (except for the tidal currents) and in comparative shelter, delicate and poorly attached forms can successfully invade the surface. Simultaneous tests of five experimental paints on the Millport raft and on a Clyde steamer showed complete failure of all five in the raft test within a few weeks, although even after 6 months the growth on the ship's test-patches was insufficient to arouse comment by the Marine Superintendent who inspected the vessel. The "voyage" in question covered the period May-October; consequently the fouling was largely algal in character, the growths perhaps being sufficient to deter the few animal forms from settling.

The *criterion of failure* of a test area by fouling should be a clearly defined "all-or-none" matter. As soon as any kind of sensitive fouling organism appears in appreciable amount on a test plate or ship, the anti-fouling mechanism has failed; it is then merely a matter of allowing sufficient time for the fouling to grow to a size large enough to be a serious impediment to a vessel. It is true that to a certain extent sub-lethal poison concentrations may retard the growth of organisms but, as growth proceeds, the organism becomes still further removed from the toxic surface and the slight initial handicap is soon likely to be overcome.

Reference has already been made to the difference in capacity possessed by different organisms to resist poisons. These variations affect the *type of fouling* developed on a poisonous plate and in many cases enable the investigator to grade a series of compositions in the order of their ability to resist fouling. Diatom "slimes" are frequently valuable for this purpose as in the absence of other forms their presence may indicate

a toxicity which is sufficient to prevent the settlement of the larger fouling organisms but which is not high enough for a wastage of poison to take place. At Millport, the continued fouling of a plate by *Amphiprora* is a useful guide to the "ideal" anti-fouling level for a composition. Since diatom slimes of this type are rarely encountered on ocean-going vessels, the fact that the composition will permit the growth of such slimes is of secondary importance; the primary feature is that the copper content (for example) is being utilized with the minimum possible wastage.

From the point of view of successful anti-fouling properties, bacterial and diatom slimes may be disregarded in the assessment of fouled plates; the presence of other larger forms is a sign of failure though even here useful distinctions may be made at lower toxicity levels. Mussels, tubeworms (*Pomatoceros* at Millport), ascidians, the brown oar weed *Laminaria*, and the green sea-lettuce *Ulva* will only grow in raft tests on surfaces which are almost non-poisonous; their presence indicates complete failure of the anti-fouling system. Barnacles are more resistant, and so is the grass-like weed *Enteromorpha*, often found at the water-line of ships; the hydroid *Tubularia* is the most resistant of all the fouling organisms that we have investigated; it will grow on paints which afford complete protection against most other types.

Toxic factors (such as the presence of copper and mercury) are not the only ones limiting the settlement of certain types although, in the long run, other surface effects do not appear to be of appreciable importance. *Tubularia* is the toughest of our fouling organisms towards copper and mercury and does not settle on certain types of *fresh* paint surface that are readily colonized by the tubeworm *Pomatoceros*, which is very sensitive to poisonous copper paints.

The failure of young *Tubularia* to settle on newly immersed paints possessing a chemically active resinous base, or a tarry or bituminous coat is quite significant, whereas the tubeworm accepts such surfaces with indifference. Whatever surface factors limit the settlement or growth of *Tubularia* on these materials, their influence must be short-lived, otherwise "non-toxic" compositions would give appreciable protection against this animal, which is definitely not the case.

The above remarks emphasize the fact that the correct basis for the assessment of a fouled surface is a qualitative rather than a quantitative one. The factor which it is required to estimate in all anti-fouling tests is the ability of the surface to prevent the settlement and growth of fouling organisms; once allowed to settle, the area covered and the size of such organisms is determined by the physico-chemical and biological environment in the neighbourhood of the exposure

raft. Such factors as season of the year, weather, sea temperature, light, competition between species, &c., will become the controlling factors, which are all quite unrelated to the anti-fouling properties of the surface itself.

The question "Is the plate fouled or is it not fouled?" may profitably be qualified by reference to the different species which are present as these differ in their sensitivity to poisons. From the biological point of view, however, the criterion is still a qualitative one; the question becomes "Can a barnacle settle on this surface?"—not "How many barnacles (or what volume of barnacle growths) have settled?"

This method of assessment of a test panel has the obvious advantage that it is independent of external biological factors and it enables the assessor to estimate what may be termed the "life" of a successful anti-fouling treatment. This "life" may be generally defined as the length of time during which the panel prevents fouling by a fairly resistant species of settler. Once the relative sensitivities of the different fouling forms have been established, an estimate of the life of a composition can be made successfully at almost all seasons of the year, although the paucity of organisms at Millport from December to February limits the use of the method during this period. Mr. K. A. Pyefinch has been largely concerned in developing this mode of assessment, and his methods, which are too detailed for this present paper, have been published * separately.

In practice the plates are now assessed for the type of organisms present and only roughly for the amount of each type, the amount being estimated so far as possible on the number of each type of organism per unit area and not on the size of the organism. The quantitative data serve mainly as a check on the qualitative picture in case of an error in assessment or where correlations of rate of development of the growth with, e.g., sea temperature, are required for other purposes.

It is obvious that quantitative measurements on fouled ships are of more value, not only because they bear a relationship to the efficiency of propulsion, but also because they provide data which may be correlated with duration of stay in ports, duration of time elapsed since failure of the anti-fouling composition, &c. Much useful data for these quantitative correlations may be obtained from exposure tests at a raft site; such data, however, are irrelevant to the problem of assessing the performance of anti-fouling compositions in a raft test, and can equally well be obtained from studies on non-poisonous surfaces.

Dr. M. F. Spooner is at present working on the problem of fouling assessments on ships; her work will be published in a later report.

(5) FURTHER WORK ON FOULING ORGANISMS.

It will be useful at this point to discuss briefly some of the more recent work carried out at Millport on the different types of organisms responsible for fouling.

(i) *Bacterial Slime.*

This work has been largely carried out by Dr. M. F. Spooner, who has studied the bacterial slime in some detail.

This bacterial layer has been held by some investigators to be an important precursor of the later fouling growths, providing a necessary substratum on which seaweed spores and animal larvae may settle and grow. This is untrue. Several species of seaweeds, the hydroid *Tubularia*, and the barnacle, can attach to surfaces which carry no slime film. The most convincing demonstration of this has been the settlement within 3 hr. of a considerable colony of the common fouling seaweed *Enteromorpha* on a clean glass surface. Within such time no development of a slime "layer" could possibly have taken place.

The reasons for postulating the necessity of a preliminary slime phase have never been clearly indicated. There can be no cogent nutritional reason for such a causal sequence since the plant settlers derive all their nutrients from the sea and most of the animal forms do not feed at the time of settlement. The idea that a slime film is needed to anchor the spores and larvae is equally unfounded as they are so small in size that they will lie well within the layer of laminar flow on the surface and, within a distance of less than $25\ \mu$ † from the surface, the water velocities and shearing forces tending to remove the animal or plant must be very low indeed. For the larger settling forms—particularly the barnacle with a size of 1 mm. at settlement—the problem of water flow is more important, but slime is not necessary for the settlement of the cyprid as it has a very efficient "sucker" mechanism for preliminary attachment.

Slime can delay the onset of permanent fouling by stripping, together with the insecurely attached organisms. On some paints—particularly those containing a rosin-wax mixture—the process of slime formation and stripping is continually repeated, whereas on most other paints new slime formation after stripping is much slower than at first, enabling larger fouling organisms to gain a secure foothold.

Slime may be avoided by some animals. This has been observed for barnacle cyprids and also for tubeworms, both of which tend to avoid surfaces coated with slime films, but which settle heavily on adjacent areas relatively free from slime.

* K. A. Pyefinch, *Journal of The Iron and Steel Institute*, 1945, No. II., p. 229 p.

† $25\ \mu = 0.001\ \text{in.}$, approximately.

In cases where the presence of an irregular gelatinous layer of slime may accumulate spores of fouling organisms, one may expect heavier fouling growths in consequence. Owing to the permanence of the slime layer and to the fact that the conditions at the surface of such a slime are not particularly favourable to growth, there is no reason to suggest that the *growth* of heavy fouling should be any better on slime than over surfaces which were not heavily slimed, and this is certainly true in practice.

There is no obvious correlation between slime formation and anti-fouling efficiency. Tests carried out on a large variety of paints show, for example, that rosin-wax mixtures slime heavily and foul equally heavily, but non-reactive synthetic resins (*e.g.*, coumarones, *esterified* rosin-modified phenolics, &c.) and glass produce a negligible slime and yet foul very heavily. Among poisonous paints, phenyl mercury pigments in rosin-based media show very heavy slime formation with little or no fouling, while copper paints which prevent fouling do so with the minimum amount of slime formation.

The above statements refer particularly to bacterial slime, which appears to be uniform in character. The diatom slimes, which are described later, can be qualitatively related to the anti-fouling performance of the paints on which they grow.

(a) *The Bacterial Slime Production in Relation to Paint Constituents.*

Slime production on non-toxic panels is very clearly related to the rosin in the paint. The figures given below of the slime production on pure ingredients and on simple mixtures show that an admixture of rosin with oil or wax reduces the amount of slime formation, while the presence of pigment increases it—presumably by increasing the penetration of the “paint” surface by the sea-water. Hydrated iron oxides of high oil absorption give heavier slimes than, *e.g.*, magnetic iron oxide which has a much lower oil absorption :

Variable Ingredient.	Proportions.	Effect on Slime Production, arbitrary units of slime thick- ness per slide.	
Rosin . . .	100%	5.4 Heaviest slime.	
Rosin/oil . . .	90 : 10	3.8 } Definite lower-	
	80 : 20	3.6 } ing.	
Rosin/oil/iron-oxide	60 : 40 : 20	5.3 } Pigment appears	
	50 : 50 : 50	5.3 } to increase the	
	33 : 66 : 80	5.3 } availability of	
			} the rosin.
Rosin/paraffin-wax.	50 : 50	1.7 Definite lower-	
			} ing.
Paraffin wax . . .	100%	1.2	
Paraffin-wax/oil . . .	50 : 50	1.6	
Beeswax	1.4	
Lanolin	1.3	
Naphthalene *	2.3	

* Naphthalene forms exceedingly heavy slime in the tank circulation at Plymouth but its slime production at Millport is negligible in comparison.

On actual paints pigmented with black hydrated iron oxide, the slime formation was high with rosin-oil varnishes, lower when lanolin, naphthalene, paraffin wax, or coal-tar pitch was added, and almost negligible when the rosin was replaced by coumarone, rosin-modified phenolic resins, or bitumen.

A series of experiments on the growth of slime films on pure resins showed that the main factors concerned in slime growth were acidity and chemical stability, which presumably determine the degree of solubility of the resin in the alkaline sea-water and therefore the extent of the bacterial attack. The amount of slime growth formed on various surfaces was :

	Units.
Rosin	4-6
Acid rosin-modified phenolics	1.5
Esterified rosin-modified phenolics	} 0.5
Ester gum	
Glass	

It is clear that most anti-fouling paints, since they contain considerable quantities of rosin, are potentially heavy slime-formers. This explains the tendency for such a paint to develop slime at an early stage in its failure as an anti-fouling paint, especially since the bacteria can survive fairly high copper concentrations. The sequence bacterial slime → diatom → seaweed, which is so characteristic of the later life of an anti-fouling paint is almost certainly the result of the high rosin content of the paint and the graded poison sensitivity of the three phases.

(b) *Relation of Slime to the Poisons of the Anti-Fouling Paint.*

The results above have been mainly concerned with the action of slime on a non-poisonous surface and the development of later fouling. It was thought not impossible that the slime on a toxic surface might contribute appreciably to the anti-fouling action; experiments were therefore undertaken to test this possibility.

Rosin-coated slides on which a bacterial slime film had been started were hung in copper solutions in sea-water for 2-3 weeks. At low copper concentrations (0.5 parts per million) the copper rapidly disappeared from the sea-water and was found, by analysis, to be distributed more or less equally between the slime, the rosin, and the bacterial scum on the wall of the culture bottle. The slimes contained about 1 $\mu\text{g.}/\text{sq. cm.}$ of copper, or about 1-10 parts per million of copper on the dry weight of the slime. In higher copper concentrations or in culture vessels where the copper concentration was maintained by the repeated addition of copper, the slime film took up no additional copper but considerable quantities were taken up by the rosin, which became green in colour. Such slides, when soaked in stirred sea-

water, maintained a steady but very low loss of copper into the sea-water for many days but this was far too little to have any anti-fouling effect.

It has been found (*see* p. 315 P) that the anti-fouling effect of a patch of toxic paint frequently extends well beyond its borders. The opportunity was taken to see how much copper a rosin slime would pick up from an adjacent toxic painted slide in the sea. A sequence of slides showed the following results:

R.S.	R.S.	→			R.S.	R.S.
20	72	T.P.	T.P.	T.P.	99	68
			

R.S. = Slide coated with slimed rosin. (Copper contents are given in microgrammes per slide.)
T.P. = Slide coated with a cuprous oxide anti-fouling paint.

The tidal flow at the Millport raft is asymmetrical, the principal direction being shown by the arrow above. The copper contents of the slime were of the same order as in the laboratory experiments.

The most convincing evidence against the usefulness of copper-containing slime as an anti-fouling agent is derived from leaching studies where the anti-fouling property of a copper paint is found to be dependent solely on its rate of loss of copper and does not depend on the degree of slime formation. It is evident that the poisonous action from the steady stream of copper leaching out is of very much greater efficacy than the very small amount probably present in the slime film. A further point is that leaching of these copper-soaked slime-films produces little or no copper into sea-water at ordinary pH values, and it is difficult to see how far such copper can be made "available" to the organism.

Animals, of course, may feed on the slime and take in copper in this way, but, from the very low copper-content figures above, it seems unlikely that any appreciable poisoning can result from this.

(ii) *Diatom Growths.* (F.S.B.* Figs. 31, 32, 40.)

A very large number of diatom species have been recorded in fouling growths, but many of these are passengers rather than attached fouling forms. At Millport, during the spring, numerous floating diatoms occur and may become entangled with the debris and slime on the surface of the plate. These forms usually die away during April and their place is taken by genuine "fouling" diatoms which are attached to the paint surface. A third group of diatoms—the *epiphytic* forms—grow on other fouling organisms, particularly on those having a filamentous or branching structure

(such as seaweeds, hydroids, or even other diatom chains). Some of these epiphytic forms will, however, also grow attached to the paint surface.

Among the truly attached or fouling diatoms, four are sufficiently common to rank as important constituents of the fouling, particularly during the early stages of growth on a panel. These four are members of the genera *Achnanthes*, *Amphiprora*, *Fragilaria*, and *Schizonema*. The last two grow in filaments looking rather like brown seaweeds, while *Achnanthes* appears rather like a grey pile on a carpet; *Amphiprora* always forms a characteristic brown "slime" on the paint surface. *Schizonema* can also grow in an adherent mucous slime without forming filaments.

From the practical point of view, diatoms are probably not an important fouling constituent though Dr. G. S. Baker has suggested that "slime" can appreciably increase the skin friction of a vessel. The usefulness of diatoms in work on anti-fouling methods lies in their value as indicators of the efficacy of an anti-fouling surface—especially with copper and mercury paints. In particular, *Amphiprora* grows extensively (from April onwards) on paints which are sufficiently poisonous to prevent all other types of organisms from settling successfully. A copper-mercury composition which permits patches of *Amphiprora* (and nothing else) to grow on it can be relied on to prevent fouling without wasting its poisons by discharging them at an excessive rate.

Achnanthes and *Schizonema* are more sensitive and will grow in association with the fouling seaweeds; the former has in addition a specific preference for certain types of paint matrix which render its occurrence somewhat unpredictable; it seems frequently to occur on paints based on waxes or metallic soaps. *Fragilaria* is slightly more sensitive but its very rapid rate of growth makes it a very suitable test organism to measure the effectiveness of a paint during the early stages of life in a raft test. Its limited season (July–August) at Millport rather diminishes its usefulness for this purpose.

(iii) *Algal Growths* ("Seaweeds").

Very few species of seaweeds appear on fouled ships in appreciable amounts. The examination of several hundreds of samples suggest that *Ectocarpus* and *Enteromorpha* (F.S.B. Figs. 2, 6, 28, 38, and 41) are the principal constituents of the water-line fouling, the latter forming the bulk of the weed fouling on all ships.

A much greater variety of seaweed fouling occurs on panels exposed in raft tests; this varied

* In this and later sections of the report illustrations of many of the forms referred to are given in the paper "Fouling of Ships' Bottoms: Identification of Marine Growths," by the Marine Corrosion Sub-Committee (*Journal of The Iron and Steel Institute*, 1944, No. II., p. 143 P). References to these illustrations are preceded by the letters F.S.B.

flora is probably related to the more favourable conditions for settlement on specimens exposed near a heavy source of infection by many different species, and also to the low maximum water velocity (equal to the tidal current at the raft site) which allows seaweeds to become established in the raft tests whereas they would be torn off at the speed of movement of a ship.

At Millport the algal colonizers of the plates can be generally classified according to their season of *settlement*, although they all grow most rapidly during the summer.

Ectocarpus, *Enteromorpha*, *Cladophora* (F.S.B. Fig. 4) and *Ulva* (F.S.B. Fig. 3) can settle all the year round, but the amount of settlement in the winter months is generally small.

Ulothrix (F.S.B. Fig. 29) (March–October), *Polysiphonia* (F.S.B. Fig. 8) (February–September), and *Laminaria* (F.S.B. Fig. 5) (December–March) all have a well-defined season of settlement so that a panel immersed outside this period will not collect these weeds until the settling season commences.

Ceramium (F.S.B. Figs. 7 and 42) is a red seaweed which occurs commonly at the Caernarvon exposure station but less frequently at Millport. It appears to settle most freely in September and October but will also colonize a surface from this period until March at least. During the summer it does not settle at Millport on freshly immersed surfaces.

From the point of view of the usefulness of these seaweeds in estimating the efficiency of anti-fouling compositions, their sensitivity to poisons varies widely. *Ulothrix* (a hair-like green filament composed of a single row of cells) is the most resistant of all the seaweeds to copper and to mercury. It will grow on compositions which will give protection against all the larger fouling forms.

Enteromorpha—the “grass” most commonly found at the ship’s water-line—is more sensitive to copper than is *Ulothrix*, and much more sensitive to mercury. It is probably for this reason that mercury is often used in the water-line region as an algicidal paint constituent, although an adequate copper toxicity can completely eliminate the need for mercury if considered solely from this point of view.

Enteromorpha and *Ulothrix* are very markedly affected in their growth by light intensity. Not only do they grow much more rapidly very near (0–6 in. in depth) the water-line at Millport, but they are much more resistant to poisoning under such conditions. Thus, while on a non-toxic plate they will both occur down to a depth of 4–6 ft., on a plate having a fairly high degree of toxicity their density will fall off rapidly at depths below 2 ft.

It is probably for this reason that *Enteromorpha* is such a common water-line fouling form. The

more effective the anti-fouling composition, the shallower will be the belt of *Enteromorpha* at the water-line until, of course, at a sufficiently high toxicity it will disappear altogether.

Under optimum light conditions *Enteromorpha* is one of the most resistant of the large fouling organisms. It is not surprising that ships when dry-docked are often found free from all fouling except this water-line “grass.”

Ectocarpus, a brown tufted seaweed, is also very resistant to copper but is much less sensitive to light intensity and, as it occurs all the year round to a greater or lesser extent, it is by far the commonest fouling seaweed found on test panels exposed at Millport. A non-toxic test panel immersed at the appropriate time of year will show *Ectocarpus* and *Enteromorpha* both occurring down to a depth of several feet, but the green *Enteromorpha* will be much denser at the surface. If the panel is fairly poisonous the *Enteromorpha* belt will be reduced to almost negligible proportions at 2–3 ft., while *Ectocarpus* will survive much deeper.

A very frequent type of algal fouling at Millport occurs in the form of small “brown mats” strongly adherent to the paint surface and particularly common on paints containing copper compounds as the only toxic pigment. These brown mats appear to be a composite growth, according to Professor F. E. Fritsch, who has suggested that, as well as flattened growth of *Ectocarpus*, they contain a number of related algae such as *Myrionema* and possibly *Hecatonema*. The occurrence of these mats without other fouling is a clear indication of a high level of copper toxicity—sufficient, in fact, to prevent fouling by all the larger organisms except possibly the hydroid *Tubularia*. Other species do not settle freely on a *continuous* brown mat layer but, if space is available for colonization by other species which are in fact absent from the fouled surface, these brown mats form an excellent indication of a definite stage in the decay of the anti-fouling properties of a composition.

All the other seaweeds mentioned are much less resistant to poisons; the green *Cladophora*, the red *Polysiphonia*, and *Ceramium* will grow on slightly poisonous paints, but the presence of *Ulva* (the sea-lettuce) or *Laminaria* (the large brown oar weed) indicates an almost complete lack of toxicity in a paint.

(iv) *Animal Fouling Organisms.*

(a) *Barnacles.** (F.S.B. Figs. 12 and 21.)

The barnacle is undoubtedly the most important of all forms of fouling. It is relatively highly resistant to poisons, and feeds at a considerable distance above its substratum so that, once it has

* The greater part of this work on barnacles has been carried out by Mr. K. A. Pyefinch.

settled, it is impossible for it to be dislodged by any poisonous paint, as it has a firm attachment of very large area and a shell which persists even after the organism dies; from the point of view of creating a permanent resistance to motion, it is by far the most serious of all the forms settling on a ship.

In soft paint films the conical shell of the barnacle "burrows" into the film by the mechanical chiselling action at the growing base. This growth lifts the paint film from the metal in the same way that such a film will climb on to a paint scraper. Ultimately a barnacle with its conical sides covered with paint may be found to have chiselled-down almost to the metal substratum by this process.

The conical shell characteristic of the isolated individual becomes elongated in a close-packed colony. New barnacle settlements can grow on the older members of a colony and masses several inches thick may result. The growth rate is extremely rapid, a few months in temperate climates being sufficient to cover the plating to 1 in. in depth; in the tropics, still larger forms occur and grow even more rapidly.

At Millport, two principal species are encountered. The first to settle is *Balanus balanoides* which is the intertidal shore form of acorn barnacle universally occurring on British coasts. This species is not so frequently found on ships as the smoother-shelled (and inappropriately named) *Balanus crenatus* which is found on the shore almost entirely below low-tide level. The two species settle at different times of the year, but appear to have much the same resistance to anti-fouling poisons so that raft tests can be relied on to give a true estimate of paint performance whichever form is present.

A.—*Season of Settlement and Life History.*—*Balanus balanoides* settles at Millport over a very restricted period of the year. The settlement is almost confined to April, in which month and at suitable sites near the shore, one may encounter up to 100,000 larvae/cu. m. in the surface seawater. Although its natural shore habitat is between low- and high-tide level where it is alternately submerged and exposed to the atmosphere, it will readily settle on completely submerged panels.

The adult barnacles spawn in March, producing broods of active nauplius larvae (the eggs hatch inside the parental cavity and as each barnacle is hermaphrodite, though cross-fertilized, every adult barnacle will produce up to 10,000 of these larvae at one spawning). The free-swimming nauplii are carried about by the tides and currents, feeding on minute plant life and passing through six moults—like a caterpillar. The last moult produces a seventh stage, the cypris larva, which corresponds roughly to the "pupal" stage of an

insect in that it does not appear to feed. The cypris stage, however, is an active one, during which it swims by means of its legs or "walks" on submerged surfaces by the antennae at the head end. Large amounts of oil globules in the head region may be a food reserve and would also increase the buoyancy of the animal.

The cypris stage of *Balanus balanoides* may persist for a week without settling. When settlement occurs, the sucker-like tips of the antennae become firmly attached to the substratum. A cement gland in the head secretes through the antenna a protein cement which hardens by a tanning process similar to the tanning of leather; the animal moults and assumes the final barnacle form within 48 hr. Lime is laid down in the initially horny shell, and the animal, lying on its back in this shell, feeds by protruding its six pairs of legs as a casting net.

The larvae of *Balanus crenatus* hatch and pass through a similar metamorphosis rather later in the year and over a much longer period. The cypris stage occurs at Millport from March to September and settlement can take place throughout that period. The number of *B. crenatus* settling on the Millport raft specimens is of the same order as that of *B. balanoides* but no very large concentrations of cyprids have been encountered.

An interesting difference in the behaviour of the two species of cypris is probably connected with the distribution of adults on the shore. It is unlikely that either can attach to a substratum at any appreciable water velocity; it would seem that even the normal tidal flow ($1\frac{1}{2}$ knots) is too high and that settlement takes place almost entirely at slack water. But once a temporary attachment (by means of the antennal suckers) is achieved, rapid water flow will not dislodge the cypris of *B. balanoides*, while that of *B. crenatus* loosens its hold and the animal is washed away. Since the *B. balanoides* cypris is attracted to light, it swims up to the surface and, when washed up by a wave on the shore, hangs on firmly in spite of water motion; its "preference" for intertidal settlement can thus be largely explained. The *B. crenatus* cypris deposited under such circumstances will fail to adhere and there is also evidence that its reaction to light may differ from that of *B. balanoides*.

Laboratory experiments suggest that, once attached, the cypris of *B. balanoides* can, with the aid of its sucker alone and without relying on "cement," resist a water flow of more than 15 knots without becoming detached.

As is well known, barnacle larvae tend to become attached in grooves or depressions in the surface; such a site is probably selected by the cypris in the course of an exploration of the substratum, i.e., by "walking" about on its antennae until a favourable site is reached.

B.—*Growth Rate*.—Individuals of *B. crenatus* on panels immersed at Millport may grow to $\frac{1}{2}$ in. in dia. in 2 months and, when not crowded together, to 1 in. in dia. in 5 months. This growth rate may be retarded on poisonous paints, though probably only in the early stages.

On the whole, thick growths of algae discourage the successful colonization of a panel by barnacles; such growths interfere with the cyprid settlement, but they also prevent the young and even the adult barnacles from feeding properly; many small dead barnacles are often encountered on a panel heavily fouled with algae.

C.—*The Settlement of Barnacles on Poisonous Paints*.—On panels coated with anti-fouling compositions, barnacles will settle at higher levels of toxicity than will many other forms. It has often been stated that unless an anti-fouling paint actually prevents settlement by repelling or poisoning the larval settling stage it cannot be an effective preventive against fouling. This is only partly true for these animals. The exceptionally heavy 1944 settlement of *B. balanoides* at Millport plastered almost every plate on the raft with cyprids, most of which successfully metamorphosed into young barnacles. On paints of sufficiently high toxicity these small barnacles all died and ultimately washed off the paint surface; this suggested that only the initial limited attachment by the antennae and its pre-metamorphosis envelopment of cement had become effective; the later extensive cement secretion over the whole base had not taken effect.

The barnacle cypris is one of the largest fouling organisms at the time of settlement; it appears large enough to interfere with the laminar flow over the plate surface and it is an undoubted fact that, in a tidal flow, such as that on the Millport raft, barnacles will settle successfully on a fairly toxic surface on the downstream side of an obstruction—even that provided by another barnacle larva.

(b) *Tubeworms*.^{*} (F.S.B. Fig. 11.)

Two species of tubeworms are principally responsible for fouling in this country. One of them, *Hydroides norvegica*, only rarely occurs on the plates at Millport; the other, *Pomatoceros triqueter*, settles there in considerable numbers from June to September. A few individuals may settle in April and May.

Their body form is a coiled calcareous tube, generally applied fairly closely to the hull surface. If the worm has had an opportunity of growing in relatively still water for a period of not less than 2 months, *Hydroides* projects out from the surface and the colony may reach a height of an inch or

more. More commonly, the movement of the water results in the tube lying flat on the hull and the resistance to motion offered by such a worm colony is likely to be much less than that of an equally dense barnacle settlement.

From the point of view of ship fouling, tubeworms may be very important. *Pomatoceros* grows only on surfaces which are almost non-poisonous; its presence on a ship's hull therefore indicates complete lack of anti-fouling properties. *Hydroides* is rather more resistant and is encountered more frequently.

One part of the underwater surface of a vessel often colonized by calcareous worms is the propeller; here its effect on ship propulsion may be very serious. It is almost impossible to anti-foul a propeller successfully as anti-fouling coatings fail to adhere under the tremendous cavitation and shearing stresses at the blade surface; thus, when the ship is in port, tubeworms readily settle on the propeller. An unpainted propeller of manganese bronze will prevent the settlement of tubeworms if the copper goes into solution at an appreciable rate; this is not likely to occur unless the metal can be insulated from the steel propeller shaft which normally acts as an anode to the bronze propeller, dissolving in the sea-water and preventing corrosion of the propeller. Whether the insulation of such a bronze propeller from the shaft is a practical proposition must be left to the naval architect.

There is no need to stress the seriousness of propeller fouling from the point of view of propulsive efficiency; the tubeworm, having a relatively thin tube with a large basal area of surface attached to the substratum, is (unlike the barnacle) not dislodged or damaged by the rotation except at the tips of the blades; consequently the fouling is very persistent.

The protection of cast-iron propellers against fouling is a difficult problem; it will be necessary to develop special high-duty anti-fouling compositions if this problem is to be solved.

A.—*Life History*.—Reference has already been made to the seasonal occurrence of the common Millport tubeworm which can settle throughout the summer. Tubeworm growth and settlement is particularly encouraged by warm temperatures, and under such conditions the fouling season may be greatly extended. Dock basins with hot-water discharges into them are thus serious potential sources of infection as has been pointed out by Dr. W. R. G. Atkins.

Tubeworms discharge their eggs into the sea where they are fertilized and develop into a free-swimming microscopic larva. After about 3 weeks the larval form passes through a metamorphosis and begins to creep about over sub-

^{*} The data on these organisms have been derived from the observations of Dr. M. F. Spooner and Miss J. C. Mott at Millport.

merged surfaces. A mucous tube forms the earliest secretion of the stationary worm; lime is laid down in the tube wall at a slightly later stage.

The adult worm feeds by bringing particles of food into the mouth from a fan of tentacles covered by microscopic vibrating hairs known as cilia. The mucus surrounding these cilia entangles the food particles which are thus directed into the mouth.

The worms can easily be reared in the laboratory as long as the larvae are fed on suitable cultures, *e.g.*, diatoms. At 16° C. the tubeworms grew in the Millport laboratory almost twice as fast as comparable specimens which were grown in the sea at 14° C. The rate of growth, however, is largely determined by the food supply rather than by the temperature and can be extremely rapid. For example, the worm tube may attain a length of $\frac{1}{2}$ in. in 1 month and of $1\frac{1}{2}$ in. by the end of 2 months in laboratory cultures.

B.—*Settlement Factors.*—The larvae of tubeworms do not appear to settle readily on slimy surfaces; it is well known that many such larvae are capable of delaying their metamorphosis until a suitable substratum is encountered. Apart from slime, however, the presence of weed or other types of fouling does not deter tubeworms, which will settle heavily at the bases of a dense weed growth. In this respect they differ markedly from the barnacles.

Tubeworms settle readily at all depths and, like barnacles, are capable of growing over the top of each other and of such shells as barnacles, &c. As a result of this a dense tubeworm settlement may be very much thicker than the diameter of the individual tubes and in tropical waters the tubeworm *Hydroides* may prove a serious hindrance to ship propulsion.

(c) *Mussels, Oysters, &c.* (F.S.B. Figs. 13 and 14.)

These "shellfish"—of which there are many different species—are common constituents of fouling wherever inferior compositions or a very extended period between dockings have rendered the ship's bottom innocuous to settlers. It is for the same reason that mussels grow in enormous masses on buoys and moorings serviced at infrequent intervals and lying sufficiently close in shore to be exposed to the settling larvae.

At Millport, mussels settle most abundantly in the autumn months. August and September are the months of heaviest settlement but it may continue until November. A light infection with larger forms is possible all the year round as larger mussels can become detached and re-attach themselves on a new substratum.

The mussel sheds its eggs into the sea where they are fertilized and develop into free-swimming

larvae like those of the tubeworms. At a later stage, however, a small shell, very similar to that of the adult, is secreted, and the "spat" settles in this form.

At the height of the mussel fouling season such a "spat-fall" will deposit hundreds of mussels per square inch on a suitable surface. Young mussels congregate around the bases of hydroids, seaweeds, &c., which form a convenient anchorage. As a result the more heavily a surface is fouled (particularly with dead or dying weed, &c., towards the end of the year) the more readily it picks up mussel fouling.

By the spring of the following year such a surface is completely covered with a dense mat of young mussels which prevent any further organisms from finding a foothold, except on the mussel shells themselves.

As they settle at Millport from late summer until the autumn months, the initial growth of mussels in the first few months is relatively slow. The mussel feeds by a ciliary action similar to that of the tubeworm, but its elaborate concentrating and sieving mechanism is totally enclosed in the shell, food currents being drawn into, and waste water pumped out of, a pair of apertures at the hind end. As little microscopic food is present in the sea in winter months the young mussel grows to a size of only a few millimetres in the first 3 months. By March, the spring outburst of marine diatoms provides an ample food supply and the mussel may attain a length of 2 in. by the time it is 9-12 months old. In warmer climates where suitable food may be present all the year round this rate of growth may be greatly exceeded.

The mussel attaches itself to the substratum by the byssus—a mass of threads secreted by the muscular foot which protrudes from the gape of the shell. Mr. K. A. Pyefinch has shown that these threads are formed from an animal "cement" secreted in the form of a thread-like protein filament; they are soft and elastic initially, but are rapidly hardened into a fairly stiff fibre by a sort of vulcanizing process analogous to the tanning of leather and already mentioned in the cement of the barnacle cypris. The mat formed by the thousands of byssus threads of a colony of mussels covers the surface of the plate with a dense feltwork, smothering all other organisms in the process and forming a very firmly adherent mass of shell growth.

It appears from its occurrence on painted panels and from a few preliminary laboratory experiments carried out at Millport, that the mussel is very sensitive to anti-fouling poisons. On anti-fouling paints, mussels fail to settle if very small amounts of copper are being liberated from the paint surface, so mussels, like tubeworms, the seaweed *Laminaria*, &c., are a good

guide to an almost complete lack of toxic properties in an anti-fouling treatment.

Mention has been made of the occasional migration of much older mussels from one surface to another. When this occurs the mussel may attach itself and grow successfully on a fairly toxic paint. This is probably due to the large size of the animal at the time of settlement, which may raise it above the toxic zone of sea-water immediately in contact with the paint. Such a state of affairs can only occur if the migrating mussel is an old one; it is never found with newly settled "spat."

One further relationship of mussels to a toxic surface is of interest. If for some reason, such as flaking of a substantial area of the anti-fouling coating, mussel spat settles in considerable numbers over a given area, the growing colony will occasionally migrate over and cover very large areas of the unflaked poisonous surface. This case is clearly analogous to the last one, in which the mussel colonizes the poisonous surface only when it is already well grown. The mass of mussels with their byssus mat may be stripped off the paint at a later stage and leave a perfectly clean surface which will not foul with other organisms, thus showing that it retains its toxic properties unimpaired.

"Oysters" of various species occur from time to time on fouled ships. The only form occurring at Millport is the "saddle oyster" *Anomia* which is recorded as occurring in summer on non-toxic plates only. It is probable that its sensitivity to poisons is similar to that of the mussel since the method of growth, settlement, and feeding of all these shellfish is essentially the same.

(d) *Hydroids*. (F.S.B. Figs. 9 and 10.)

These organisms closely resemble seaweeds to the casual observer, appearing as branched, tree-like growths. They are, however, true animals and in their occurrence, physiology, and relationship to paint surfaces, are very similar to the other animals previously described.

At least eight different species of hydroid occur on the plates at Millport, but the range of types can be best illustrated by describing two forms which are of common occurrence.

Obelia (F.S.B. Fig. 9 (top)) is a genus of which several distinct species occur on fouled plates; it is a hydroid whose commonest representative grows on the Millport panels from May to September and has its maximum occurrence in the summer months.

The animal is essentially a branching system of tubes with feeding heads at the free ends. These feeding heads, or polyps, have a mouth surrounded by a ring of tentacles which eject poisonous threads capable of paralysing or killing minute organisms which come in contact with

them. The mode of feeding and of digesting food in the body cavity is therefore essentially animal, however plant-like the organism appears.

The reproduction of *Obelia* is very different from all the forms previously mentioned. At certain points on the branching system the parent colony produces by budding a crop of small free-swimming medusae (jelly fish) which are the migratory phase in the life history. These microscopic jelly fish are of two kinds, male and female; the eggs which they produce, when shed and fertilized, develop very rapidly into a settling stage larva which grows up into the hydroid form.

The medusae of *Obelia* are found in the plankton from March until the end of the year; it is probable that this phase in the life cycle can survive for a period of several weeks as it can feed actively in the medusoid stage. During this period the organism can therefore be very widely distributed by tides and currents. The larva produced from the egg of the medusa, however, settles within a few days.

When this settling larval stage (the planula) attaches itself to a substratum, it grows into the branched hydroid with a system of basal threads spreading over and attached to the plate surface, from which other hydroid stems spring at intervals. Examination of a small plate exposed at Millport shows that from a single larval settlement an area of 6 sq. in. can be covered with a network of some 200-300 hydroid stalks within 3 weeks.

Obelia is not one of the most important fouling hydroids since it is comparatively sensitive to poisons and is therefore prevented from settling on moderately poisonous paints. Its stalks, though much stiffer than the fronds of seaweeds, can bend sufficiently to lie flat on the surface in a rapid water flow and its life appears to be rather limited. The organism usually dies off rapidly after attaining a maximum growth. The "stalks" left behind are capable of regenerating further polyps but are usually smothered by other fouling growths before this occurs.

Tubularia (F.S.B. Fig. 10) is the most resistant of all the larger fouling organisms. The general structure of this hydroid is similar to that of *Obelia*, but the basal system of threads is not so extensive. A tangled mass of small branches at the base produces dozens of thick stalks bearing only a few polyps on each stalk. *Tubularia* thus grows in very dense clumps, the pink polyp heads giving the clump a very characteristic appearance.

The life history of *Tubularia* is significantly different from that of *Obelia*; this has an important bearing on its occurrence as a fouling form. The adult *Tubularia* produces medusa buds which remain attached to the parent instead of being liberated into the sea-water as with

Obelia. These buds contain eggs which are fertilized *in situ* and the settling stage larva is released from the buds in a form very similar to that of the adult polyp. This larva settles in a relatively short time so that *Tubularia*, unlike *Obelia*, tends to be localized to the original source of infection. The very heavy incidence of *Tubularia* on panels exposed on the Millport raft is undoubtedly connected with the fact that the raft timbers are heavily fouled with it, as are the adjacent pier piles.

Tubularia occurs at Millport from April to December; its heaviest growth and settlement takes place during August-September. In a suitably mild winter it may settle and persist right through the winter until the next spring. Under unfavourable conditions the hydroid heads degenerate, leaving the stalk and finally only the branching basal system. When conditions become more suitable the stalks and polyps may be regenerated once again; *Tubularia* fouling can therefore be very persistent.

Of all the major fouling organisms *Tubularia* is the most resistant to the poisons of an anti-fouling coating. This conclusion is only partially confirmed in laboratory toxicity tests, but the results of such tests are complicated by the extraordinary regenerative power of the hydroid.

The conditions on an anti-fouling paint surface are probably such that the basal stolon is immersed in a copper solution which may be quite concentrated, but, by reason of the high resistance of this basal part, it will survive without difficulty. Polyp heads above this toxic layer will be subjected to a much lower concentration of poison and will grow and feed quite easily.

The settlement of *Tubularia* larvae can take place quite readily on surfaces which are covered with slime and, as the season of maximum settlement is so late in the year, weed fouling is rarely sufficiently dense and compact to affect the hydroid growth. Colonies of *Tubularia* are very persistent and are not likely to be smothered or reduced by any other fouling infection except perhaps by mussel growth. At Millport, however, the polyps are preyed upon by a type of sea slug which lays its eggs in very large numbers during July and August. The young slugs feed voraciously on the polyp heads and so a colony of *Tubularia* will—in spite of its hydra-like powers of regeneration—have difficulty in keeping pace with such an onslaught. This state of affairs is perhaps less likely to occur on a fouled ship unless it is in port for a considerable period.

Tubularia appears to prefer deeper water, perhaps because of the lower light intensity and the reduced wave action. Certainly the settlement is greater at 4 ft. below the surface than at 2 ft. The same is true for most fouling animals although the effect is often complicated by the

growth of algae in lighted zones which automatically tends to reduce the successful settlement of animal forms in the same area. A long plate immersed with its long axis vertical will thus tend to show algal fouling near the water surface, changing to hydroid at greater depths.

(e) *Polyzoa*. (F.S.B. Figs. 15, 23, 44, and 45.)

These are, generally speaking, not important fouling forms. Only one occurs to any extent on the Millport panels, *viz.*, *Membranipora*, which grows as a thin calcified horny crust over the paint surface and also over the shell of any animal which it encounters in its expansion. Tubeworms and barnacles may both be covered in this way.

The polyzoa are colonies of microscopic organisms, each one being of a polyp-like form. By repeated budding, the polyps form a honeycomb-like colony in which the individuals are separated by calcareous walls. The colony may lie flat on the substratum, as in *Membranipora*, or it may grow into a flat branching structure attached only at the base by a "stalk" of similar honeycomb organization to that of the rest of the colony.

The polyzoa settle in the form of free-swimming microscopic larvae. The growth of a colony is rapid and *Membranipora* is very persistent, often growing over and smothering other forms.

Probably by reason of its flattened form, *Membranipora* is extremely sensitive to poisons, and grows only on surfaces which are practically non-toxic.

(f) *Ascidians*. (F.S.B. Figs. 19, 20, and 25.)

These animals occur in many different forms on fouled panels. Some species are very large, appearing as leathery transparent bags and growing singly or in vast masses of similar individuals; others are microscopic and grow in colonies, forming slimy gelatinous growths. All feed in a similar manner by drawing into their body cavities a water current which is filtered in a complex sieve mechanism to concentrate the microscopic food in suspension.

The commonest Millport ascidian is of the colonial type and similar forms occur on panels exposed at Caernarvon and Plymouth. These slimy growths never occur on toxic panels; it seems to be a general rule that organisms such as mussels, sponges, ascidians, and even tubeworms, which feed by concentrating food particles from a continuously maintained water current, are highly sensitive to copper in the sea-water.

Ascidian fouling can be serious on a ship if the anti-fouling coating has completely lost its poisonous properties. The animals grow very rapidly indeed (preferably in dark situations) and masses from several inches to a foot in length may festoon the ship after it has lain for some time in an infested area. The resistance to motion of

such a growth is obviously enormous. However, such conditions are rarely met with in practice in view of the high sensitivity of these forms to poisons, and it is only on ships which are laid up for long periods that this type of fouling is commonly encountered.

(g) *Sponges*. (F.S.B. *Figs.* 19 and 26.)

Although they belong to an entirely different group of the animal kingdom, sponges rather closely resemble ascidians in appearance. They occur singly as small leathery bags with a large opening at the free end or in jelly-like colonies with numerous smaller openings. Feeding by means of a water current, they also are very sensitive to poisonous paints and have never been recorded except on non-toxic surfaces. They do not occur on plates at Millport, but are common on suitable panels exposed on the Sub-Committee's raft at Caernarvon.

(6) FOULING ON SHIPS.

Owing to wartime difficulties it was not possible in 1942-44 to examine a large number of vessels in dry-dock and to correlate the observed fouling with the route followed and with other relevant factors of the voyage. Several visits were made to Glasgow and Liverpool with a view to obtaining a general picture of ship fouling; for the rest it was necessary to rely on samples collected by ship-owners at the time of dry-docking.

A report by Mr. K. A. Pyefinch on the examination of some fourteen ships in dry-dock during a single visit to Liverpool gives a good indication of the type of information obtained from these inspections. From these and other observations he points out that:

(a) Water-line fouling is of almost universal occurrence; it is only very rarely or under exceptional working conditions that a ship will dry-dock without some form of water-line fouling. The usual type of weed in this zone is the green, grass-like *Enteromorpha*; *Ectocarpus* is found rather less frequently.

(b) The belt of seaweed fouling at the water-line is most clearly marked on vessels of constant draught; e.g., it is much more distinct on naval vessels than on cargo steamers. The seaweed zone is densest amidships, thinning out forward and aft, and frequently disappearing under the counter and in the bows.

(c) On merchant ships with highly variable draught a more complicated zoning of the fouling on the side is frequently found. He (Pyefinch) has divided this area amidships into the following zones:

(i) A zone of light algal fouling, extending downwards from the heavy load line. On a typical vessel this zone was about 3 ft. in depth and consisted principally of *Enteromorpha*.

(ii) A zone of heavy algal fouling (about 2 ft. in depth, consisting mainly of *Enteromorpha*).

(iii) A zone (about 18 in. in depth) of mixed plant and animal fouling, e.g., *Enteromorpha* and barnacles.

(iv) A zone of animal fouling, extending down to the bilge keel. The barnacle infection is frequently heaviest just below zone (iii) and becomes lighter towards the bilge-keel level.

Under the counter, zones (i), (ii), and (iii) do not develop and zone (iv) may reach the water-line.

(d) Bottom fouling (below the bilge keel on the flats) is characterized by great uniformity of organism and of its density. This part of the hull is almost invariably fouled by animals, the commonest fouling forms here being barnacles, hydroids, and tubeworms.

As stated above, a large part of the records of fouling on ships has been obtained from preserved samples obtained under reasonably reproducible conditions from ships in dry-dock.* Messrs. Alfred Holt & Co. have been responsible for submitting some hundreds of samples to date, together with data of the voyages, &c. A detailed study of each sample is made to determine the species present and, when possible, the order of settlement of the organisms is determined from their order of superposition. The *intensity* of fouling cannot be accurately estimated from the sample as it may vary over different areas; the Company's report is used as a basis for such a general quantitative assessment.

The detailed analysis of these samples is being carried out by Dr. M. F. Spooner, who has found it possible in many instances to determine the order of settlement and the possible origin of many of the organisms in these mixed growths. Her work will be published as a separate account at a later date. The following notes made by the author are based on a small random series of samples from 30 different voyages.

Most of the ships concerned in these 30 voyages were operating in West African waters, in the Indian Ocean, and in the Mediterranean. Only a few were on the Atlantic trade routes. Heavy fouling was experienced in 63% of the voyages which lasted for periods of 100-300 days, of which 40-200 days were spent in port. For voyages of more than 6 months in duration, 72% of the vessels

* We are greatly indebted to Mr. C. Gordon Smith for his assistance in providing this very large series of samples.

were heavily fouled when dry-docked. In only two cases were ships lightly fouled after returning from voyages of over 9 months' duration; in one of these the paint had almost completely disappeared from the plating, presumably carrying with it the attached fouling; the other vessel had probably spent 20 days in fresh water in the middle of the voyage and was very rusty, so that again loss of fouling may be suspected.

The West African coast is a well-known source of heavy fouling and it is clear from the records that barnacles, oysters, and presumably tubeworms, are all represented in this area. A voyage of only 3-4 months in this area (with a total period in port of up to 2 months) almost invariably leads to heavy fouling. The Mediterranean appears to be the source of much tubeworm fouling.

The length of stay in ports has always been known to be an important factor in determining the chance of fouling organisms settling on the vessel, but, as all the voyages concerned involved a very considerable time in harbour, this factor cannot be differentiated clearly within the present limited samples.

It is significant to note that three different anti-fouling compositions were represented in this set of data in 10, 10, and 6 cases respectively. There was no significant difference in the performance of any of the three paints used. The fact that none of these paints resist fouling adequately is a sufficient answer to critics who say that (a) there is no anti-fouling problem, or (b) the existing anti-fouling compositions are adequate to meet the requirements of the users.

III.—Chemical Studies on Anti-Fouling.

Among the numerous methods which have been suggested for preventing fouling, the only one which has become at all widespread is the painting of the ship's bottom with an anti-fouling composition. The discovery that copper sheathing will protect wooden vessels from barnacle growths was no doubt the origin of the use of copper in various forms in the earliest compositions. To-day, the use of copper, mercury, and arsenic* as anti-fouling poisons is widespread and few successful paint formulations have been devised which do not make use of one or more of these materials.

The fact that an anti-fouling paint has only a limited life and that a thin paint film has a shorter life than a thick one of similar composition suggests that the poisonous materials in the paint film disappear in the course of its "use." This has often been confirmed by such studies as those of Orton† in which the analysis of old films of

anti-fouling paint revealed little or no remaining toxic material. What is most important, however, is to decide (a) whether an appreciable loss of poison is a *necessary* feature of the anti-fouling action, and if so, (b) whether this breakdown can be used to predict the effectiveness and life of an anti-fouling composition by tests more rapid and more controllable than long-term exposure tests.

It will be of interest before going into this matter in greater detail to consider an experiment which throws a good deal of light on the mode of action of an anti-fouling paint containing only a single type of poisonous material—that most commonly used in such paints—viz., cuprous oxide.

(1) THE MODE OF ACTION OF POISONOUS PAINT COATINGS AS ANTI-FOULING AGENTS.

The two diagrams in Figs. 2(a) and 2(b) show the front and back of a single panel coated with a central vertical anti-fouling strip bordered on either side by non-toxic anti-corrosive. The paints 5M-8M which were applied in that order to the central strip contained increasing proportions of cuprous oxide. The highest copper content was at the bottom on the front of the panel and at the top on the back. The panel, which was 24 in. sq., was suspended with the top edge about 9 in. below the water surface. It was flanked on either side by similar plates so that the lower half was considerably more shaded than the upper half. Apart from the shading, the light intensity decreases in any case with the depth below the water surface.

After 31 days' exposure of the panel (at which stage the diagrams were drawn) the principal fouling organisms were of only two types, the green filamentous alga *Ulothrix*, and the filamentous diatom *Fragilaria*. Very small amounts of other forms occurred, but can be neglected in the following analysis.

It is clear that 8M is the only paint which completely prevented fouling by both organisms; 5M and 6M were fouled on both sides; 7M was slightly fouled with green *Ulothrix*, but only on the side nearest to the surface. The fouling on 5M and 6M was heavy when these patches were near the surface and included both *Ulothrix* and *Fragilaria*, while where these two paints were in the lower positions, only *Ulothrix* occurred (and to a lesser extent).

A very interesting feature of this type of experiment was the "border effect" of the poisonous paint. The anti-fouling action extended outwards beyond the poisonous paint border and so the character and amount of growth on the adjacent non-toxic paint was considerably

* Arsenic in *inorganic* form is almost ineffective as a poison, as stated in the First Report of the Marine Corrosion Sub-Committee (*loc. cit.*).

† Orton, *Journal of the Marine Biological Association*, 1929, vol. 16, p. 373.

changed. Immediately adjacent to the edge of the more poisonous paints, 7M and 8M, there was occasionally a narrow border where no fouling grew on the toxic paint. (This "clean" zone is

fouling form and relatively little *Ulothrix* occurred with it (area F).

This experiment illustrates the following points, all of which have been encountered and studied in many other exposures and laboratory tests:

(a) The poisonous action at the border of a copper paint (and therefore probably over the paint itself) is produced by a layer of poisonous sea-water which is spread over the plate by the tidal flow; *i.e.*, it is not necessary to invoke any irritant or "contact-poison" mechanism at the physical surface of the paint to account for its anti-fouling properties.

(b) The higher the copper content of the paint the more pronounced is this border effect which may extend for several inches beyond the paint boundary.

(c) The action of copper on fouling plants varies with the light intensity. A simple explanation of this could be based on the fact that these heavy metals are cumulative poisons, *i.e.*, they tend to accumulate in the organism until a copper content is produced sufficient to kill it. If the rate of growth is high in the lighter regions and lower in the darker areas (as is likely to be the case for plants) then a paint which will just poison the plant in the darker zone may not do so in the lighter zone since the plant may grow fast enough to outstrip the accumulation of copper in its tissues.

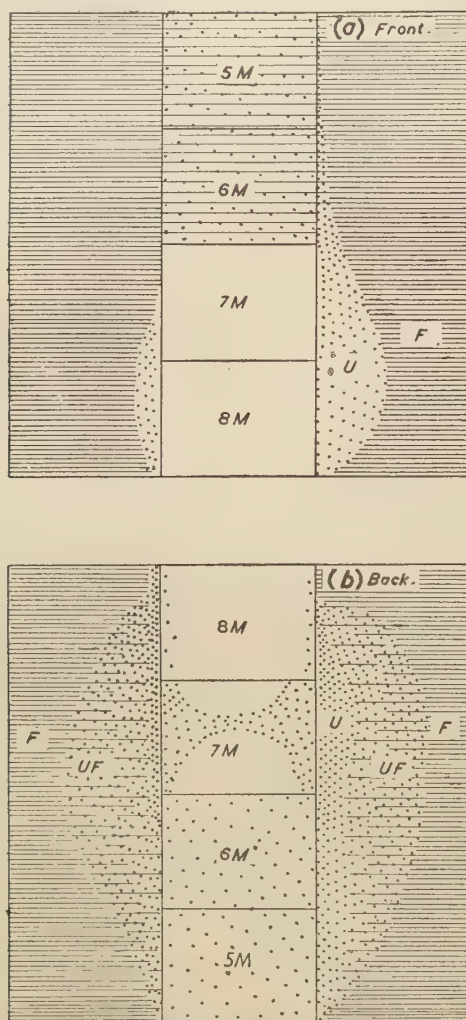
(d) Different plants show different levels of sensitivity to the copper poisoning. *Ulothrix* will grow nearer to the poisonous paint (and actually on 5M and 6M) under circumstances which will not permit the growth of *Fragilaria*.

(e) Biological competition is well illustrated in the outer parts of the non-toxic area. Where both organisms are capable of growth, as in area F, *Fragilaria* inevitably becomes the dominant form and the *Ulothrix* never becomes more than a minor constituent of the fouling. Closer to the anti-fouling paint the more toxic action of copper on *Fragilaria* reduces its growth sufficiently to permit both *Ulothrix* and *Fragilaria* to exist together. Still nearer to the toxic border *Fragilaria* becomes eliminated and only *Ulothrix* is left.

The reason for the absence of *Ulothrix* from a normal *Fragilaria* growth is obscure; the fact, however, is quite definitely established by these and other experiments.

(f) Very occasionally a border effect is seen on the anti-fouling paint surface; a toxic patch will permit *Ulothrix* to grow at its edge, while preventing growth over the main part of the area. This phenomenon is most commonly met with in copper paints and, while it is frequently shown by barnacle fouling, its occurrence in plant fouling is rare.

As far as a copper-containing anti-fouling coat-



U Zone of *Ulothrix* fouling.
F Zone of *Fragilaria* fouling.
UF Mixed fouling by *Ulothrix* and *Fragilaria*.

The two vertical zones lateral to the central anti-fouling painted area are coated with anti-corrosive only.

FIG. 2.—Fouling on and Adjacent to a Vertical Strip of Anti-Fouling Paint. 5M-8M are paints of increasing cuprous oxide content.

very much larger for some copper-mercury paints and at times extends for a distance of 2-3 in. from the border.) Outside this clean border zone was an area U almost entirely populated by the green filaments of *Ulothrix* which graded into an area UF fouled by both *Ulothrix* and *Fragilaria*. Still farther away from the influence of the anti-fouling paint, *Fragilaria* became the dominant

ing is concerned, all these facts are in agreement with the theory that the toxic action of such a paint is produced by the loss of copper from the paint film, producing over the surface a very thin layer of sea-water in which the copper concentration is high enough to poison organisms settling on the surface.

From the experiment above it is clear that the higher the copper content—and by inference the higher the rate of discharge of copper from the paint—the greater is this poisonous action; *i.e.*, it kills “tougher” organisms and the poisonous effect extends farther from the paint border. It is reasonable to expect (if a sufficiently delicate test for copper can be employed) that, within a short time, it will be possible to detect directly the rate of loss of copper into the sea-water surrounding the panel and that this rate of loss may provide an accelerated test both of the anti-fouling properties of the paint and perhaps also of its anti-fouling life.

(2) LEACHING EXPERIMENTS ON POISONOUS PAINTS.

The possibility of determining the rate of loss of copper was explored by the writer in 1941 when the anti-fouling work of the Sub-Committee was first started.* Tests were developed for copper and mercury which were of sufficient sensitivity to detect, with sufficient accuracy for the purpose required, the copper and mercury output from a paint surface into stirred sea-water within 1-2 hr. Not until 1942, however, was it possible to start a careful correlation of the results of such a “leaching test” with the anti-fouling performance of the paint. The most convincing of these early experiments is shown in Fig. 3.

For this experiment 14 paints were made all of which contained 12% of copper in the form of cuprous oxide in 14 different varnish media. A further 14 paints contained, in addition to the 12% of copper, 6% of mercury as yellow mercuric oxide in the same series of varnish media. The rates of loss of copper and mercury from these paints were measured at intervals using the methods described below. The fouling on the 28 paints was estimated from painted panels and also from painted glass slides immersed in the sea. Duplicates of the painted glass slides were used for the leaching test.

The photograph in Fig. 4 shows the appearance of the 14 paints containing cuprous oxide (without mercury) after 5 months' immersion in the sea.

* A team of workers in the U.S.A. had already at this time been carrying out similar estimations. Not until late in 1942 was an exchange of information brought about between the American and British teams, so that while the U.S.A. workers are fully entitled to claim priority for their investigation, the work described below represents an independent approach and differs appreciably in some points of technique. The first paper of the U.S. workers has just been published: Ketchum, Ferry, Riley, Redfield, and Burns, *Industrial and Engineering Chemistry*, 1945, vol. 37, p. 456.

† This figure is identical with that found earlier by the U.S. workers quoted, but was arrived at quite independently.

The fouling, which was principally diatom, seaweed, and hydroid in type, was estimated by grading the slides visually into eight different categories arbitrarily numbered 0-7. The lightest fouling observed (grade 1) was that shown by a light slime film, heavier fouling (grades 2-5) by an increasing amount of diatom and seaweed fouling, and the heaviest fouling (grades 6 and 7) by the presence of both plant and hydroid (*Obelia*) fouling.

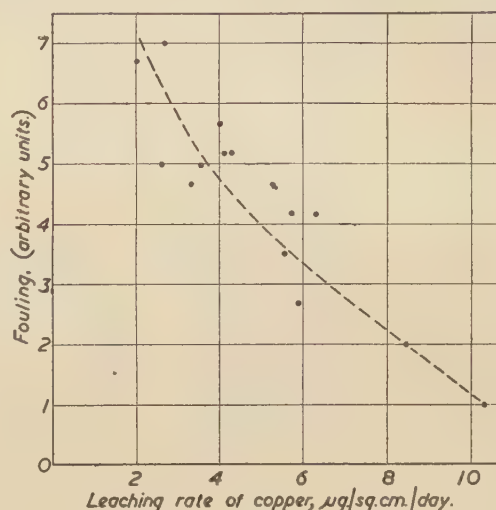


FIG. 3.—Relationship between Copper Leaching Rate and Fouling on 14 Experimental Cuprous Oxide Paints; all contained 12% of copper (as cuprous oxide), but the pigment was milled in 14 different varnish formulations.

The graph (Fig. 3) shows a clear relationship between the laboratory leaching test (actually an average of two tests each on three specimens) and the degree of fouling encountered when a duplicate sample of the paint was immersed in the sea.

The presence of appreciable fouling (apart from bacterial slime) is only encountered when the loss of copper from the painted slides is about 8×10^{-6} g./sq. cm./day or less. At a loss of $10 \uparrow \mu\text{g./sq. cm./day}$ fouling is negligible and later results have confirmed this result over a wide range of paints in which the only anti-fouling poison contained was copper.

In Fig. 4 the two uppermost slides of each group of six show the effect of introducing mercuric oxide (6%) into the same series of paints. It would appear that in the presence of mercuric oxide the rate of loss of copper required

to render a paint anti-fouling is appreciably less than that required when the same paint medium contains copper oxide as its only poison. The leaching rate of mercury from the copper-mercury paints was very variable and curiously unconnected with the anti-fouling efficiency but, provided that an appreciable quantity of mercury (at least $\frac{1}{2}$ $\mu\text{g.}/\text{sq. cm.}/\text{day}$) was escaping, it seemed that a copper leaching rate of 5-7 $\mu\text{g.}/\text{sq. cm.}/\text{day}$ was sufficient to indicate satisfactory properties of the paint. This result requires further interpretation in the light of recent work by Dr. H. Barnes on the mercury leaching rate

Fig. 5 shows in a diagrammatic form the correlation between leaching rate and fouling on a number of *commercial* compositions recently tested at Millport. The fouling was estimated on painted panels heavily protected against corrosion (as on a vessel with a "built-up" paint coat resulting from several repaintings) by several coats of the commercial painting system. The results on four of the paints have been omitted; from these four, leaching tests also showed the loss of a supplementary poison in the form of an *organic* arsenical compound. Reference to leaching tests on one such poison is made later in the text.

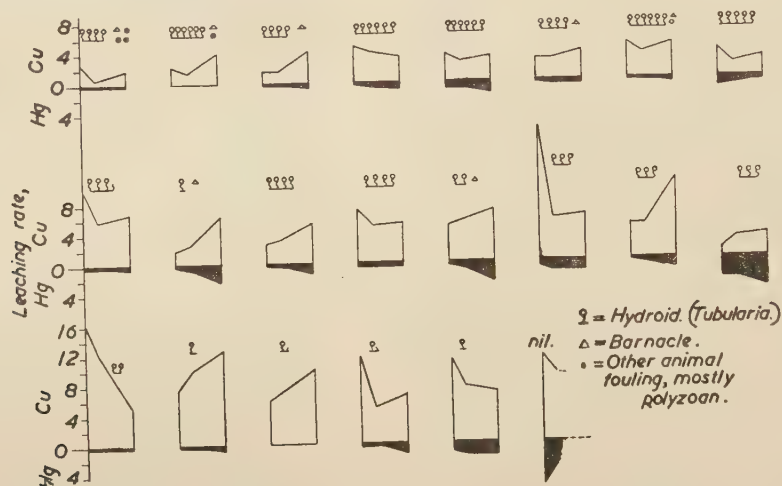


FIG. 5.—Comparison of Fouling and Leaching Rate for 22 Commercial Anti-Fouling Compositions. Each figure shows above the zero line the copper leaching rate at 30, 60, and 120 days after immersion, and below the zero line (the black area) the corresponding mercury leaching rates. The symbols above each figure represent schematically the type and amount of fouling on the panels after two months' immersion in the sea. The three rows correspond approximately with the categories: Heavily fouled, moderately fouled, and slightly (or negligibly) fouled.

of paints containing mercuric oxide, and little importance should be attached to the quantitative data on such paints.

The copper and copper-mercury paints used in the above experiment were all made with very short oil-resin varnishes. Leaded linseed-oil was used throughout in the proportion of 1 part of oil to 4 parts by weight of the resin. The resins used were rosin, ester gum, acid and neutral (esterified) rosin-modified phenolics, straight phenolics, coumarone resin, and blown bitumen. To certain of the rosin-oil varnishes were added lanolin, paraffin wax, naphthalene, and coal-tar pitch. The paints and varnishes were all made on a laboratory scale at Millport and it is admitted that on grounds of durability and suitability for anti-fouling purposes they left much to be desired. The correlation, however, between the leaching results and the anti-fouling performance of the paints is beyond question and has been confirmed by later experiments based on formulations prepared by experienced paint technologists.

(i) Leaching Technique.

The technique for studying the leaching rate of these paints has varied slightly in the past 3 years. It would be pointless to describe the course of development of the methods used; the following account represents the practice adopted for the 1943 tests.

(a) Test-Slides.

The test-slides were of ground glass (3×1 in.) painted front and back over an area of 4 sq. in., leaving an unpainted gap of $\frac{3}{8}$ in. at the bottom and $\frac{5}{8}$ in. at the top. The slides were weighed before painting and again after painting with a single coat of the anti-fouling composition under test.

After a drying time of 6 hr. under indoor conditions (at a temperature of $10-15^\circ \text{C.}$ and relative humidity *circa* 65%) the slides were hung on a linen or a glass or polyvinyl-acetate thread looped round the unpainted top end and were immersed in a tank of running sea-water.

Leaching tests were carried out after 3, 10, 30, 60, 120, and 240 days' immersion and at other times if the leaching curves indicated the possibility of interesting results.

It will be noted that no anti-corrosive undercoat was employed. Tests made on durable anti-fouling paints showed that the leaching rate was not materially affected by the presence of an undercoat, as shown by the following results:

Paint.	A.	B.	C.	D.	E.	F.
Leaching rate without undercoat .	2.4	6.8	4.8	1.5	6.7	2.5
Leaching rate with undercoat .	1.7	5.5	4.5	1.5	5.7	2.9

The adhesion of the paints to a ground-glass surface was excellent; the coatings were usually intact for at least as long as they would be over anti-corrosive undercoats and sometimes for very much longer, if the lack of adhesion of the anti-fouling to the anti-corrosive coating is poor.

(b) The Leaching Test.

In order to carry out a leaching test, the slide is immersed in 60 ml. of fresh (filtered) sea-water in a specimen tube, $4 \times 1\frac{1}{2}$ in. in dia., the whole of the painted portion of the slide being under the

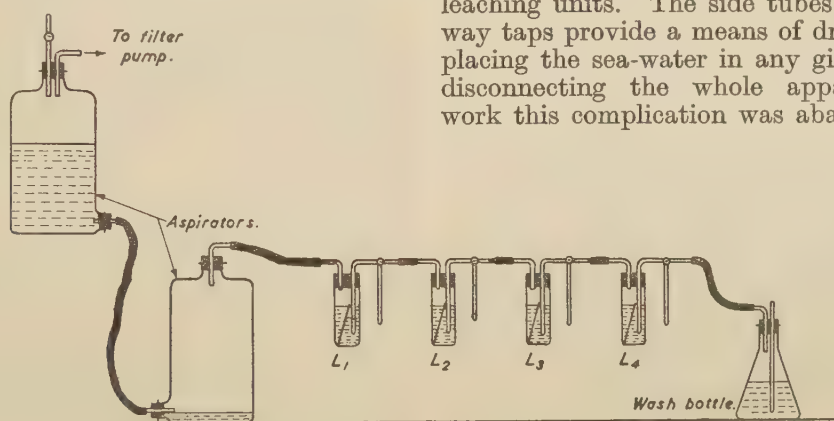


FIG. 7.—A (Shortened) Bank of Leaching Units, L_1 to L_4 , connected in series. The wash bottle contains sea-water. The aspirators were used to produce the pressure needed to empty the leaching tubes. The latest apparatus eliminates the use of the aspirator and maintains six banks of units in parallel on six matched filter pumps run from a constant water head.

surface of the water. Air is bubbled through the sea-water by suction from a filter pump.

A single leaching unit of an early type is shown in Fig. 6. The air bubbles through the apparatus to stir the sea-water continuously as well as to keep it aerated, and the conditions to which the paint is exposed thus correspond roughly to those which a panel would experience in the open sea. Twelve to fifteen such leaching units are connected in series and six similar banks of units can be run from six matched filter pumps supplied from a constant water-head of about 6 ft. The rate of bubbling in all the units is thus kept substantially

constant and up to 90 experiments can be carried out at one time. The incoming air in each bank is first bubbled through a wash bottle containing

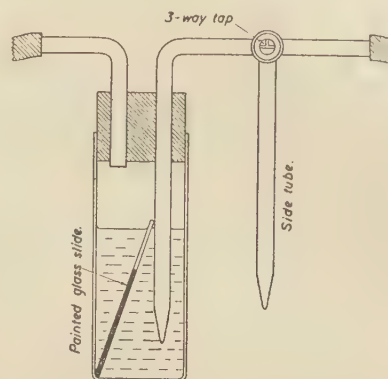


FIG. 6.—Leaching Unit Employed in the Test Described in the Text. In later models the T-tube on the right was discarded; it was employed originally as a means of emptying individual leaching units.

sea-water, which prevents evaporation of the contents of the leaching tubes by the stream of air bubbles. Fig. 7 represents a typical bank of such leaching units. The side tubes with their three-way taps provide a means of drawing off and replacing the sea-water in any given tube without disconnecting the whole apparatus. In later work this complication was abandoned and each

unit was fitted with a simple pair of tubes without the T-piece.

The temperature during the 2-hr. leaching run is usually kept within one or two degrees of 15°C . when possible, though thermostatic control has not been found necessary for ordinary experiments. The pH of the sea-water remains substantially constant during the experiment.

Since the sea temperature at Millport rarely exceeds 13°C ., the temperature as well as the character and intensity of stirring and aeration are not identical with the conditions of exposure in the sea. This does not destroy the usefulness

of the test, which is concerned with finding a laboratory performance test that can predict the anti-fouling properties of the composition when it is immersed in the sea. The limitations of the test from this point of view are discussed later (see p. 324 P).

After 2 hr. the units are disconnected and the slides removed. The 60-ml. sample is halved, 30 ml. being used for the copper estimation and the rest, if required, for the mercury estimation.

(c) *Estimation of Copper in the Leachates.*

A.—*Direct Technique.*—To the 30 ml. of leachate, 2 ml. of a 0.1% solution of sodium diethyl dithiocarbamate in distilled water are added, the solution then being made up with sea-water to 40 ml. After 15 min. the absorption of the yellow colour is measured on a Hilger Spekker absorptiometer with a spectrum violet filter (4500 Å.) using a "flow-through" cell. The latter enables a long series of leachates to be analysed in succession without the need for removal of the cell from the apparatus for cleaning; as long as successive solutions are not widely different in copper concentration, errors due to contamination with previous samples are very small. An experienced operator can handle 100 samples in 1 hr.

The thiocarbamate solution must be reasonably fresh although if older than a few days it can still be used if more than 2 ml. are added. It has been found that even the dry reagent deteriorates after several months. With 2 ml. of fresh reagent solution the copper calibration curve is linear up to 50 µg. of copper (= 45 µg./sq. cm./day copper leaching rate for a standard leaching slide). Provided that the colorimetry is carried out within $\frac{1}{2}$ hr. of adding the reagent, the colour is sufficiently stable not to require the addition of a protective colloid such as gum arabic, and the buffering power of the sea-water ensures that the pH at which the test is carried out is constant.

For routine tests where extreme accuracy is not essential, the above very simple technique is perfectly adequate for satisfactory results; as many as 200 complete leaching tests per day have occasionally been made at Millport with this method. More time is consumed in cleaning glassware than in carrying out the actual test as, owing to the small amounts of copper being studied, scrupulous care in the chemical cleansing of all glassware used is absolutely essential.

Complications arise (1) where zinc may be present in the leachates, and (2) where the leaching slides may have accumulated heavy slime. Zinc reacts with dithiocarbamate to give a white turbidity although it is very rare for this metal to be present (even in a zinc-oxide-pigmented paint) in sufficient quantity to interfere with the determination. Zinc diethyl dithiocarbamate is not precipitated if the leachate is rendered alkaline

by adding 2 ml. of 3N ammonia before the 2 ml. of reagent is added. A prior addition of 2 ml. of ammonium citrate solution (20% in distilled water) prevents the formation of alkali hydroxide precipitate on addition of the ammonia.

One of the most troublesome features encountered in leaching tests at Millport has been the almost invariable development of a heavy slime coating on slides stored in the sea-water tanks. The fact that such slimes develop on rosin-containing paints has already been referred to in an earlier section of this report; the bacteria concerned appear to be present in very large numbers in the Millport sea-water tanks. Within a week or two, leaching slides—particularly if their copper leaching rate is low—may become covered with slime which strips off during the leaching test and produces an appreciable turbidity. At first this slime was simply brushed off, but it was found (a) that brushing, unless it was very severe, did not remove all the slime, and (b) severe brushing seriously affected the subsequent leaching of copper from the slide, at times doubling or even trebling the leaching rate observed.

The standard practice later adopted for all such routine tests was as follows:

At the first leaching on the third day after immersion no special precautions were taken as no slime had developed; at all subsequent leachings the slide was removed from the tanks and soaked in a 4% solution of neutral formalin in sea-water for 24 hr. This killed the slime-forming bacteria and loosened the adhesion of the slime considerably. On removal from the formalin tank the slides were given a light brushing; they were then returned to the running sea-water tank for a further 3 days before the actual leaching test.

It was found, in the case of slides which had been in the running-sea-water tank for 30 days or more, that this formalin and brushing treatment did not affect the leaching rate. There is some reason for believing that at 10 days the above technique does slightly increase the rate of loss of copper. Even for slides older than 10 days, complications occasionally arose with paints containing little or no rosin and which relied on very high copper contents to produce a leaching rate. For example, a linseed-oil/coumarone varnish pigmented with sufficient copper to give a high *early* leaching rate may fall off to a leaching rate of only 2 or 3 µg./sq. cm./day in the course of 20 days. Brushing such a composition occasionally doubled its leaching rate at that stage or later in its life. The reason for this anomaly will be discussed in a later communication; it is sufficient to point out that paints of this type have never proved to be satisfactory as anti-fouling compositions, and a repeat of the leaching test

after a few days without further brushing readily established the anomalous result which, however, is not persistent.

B.—*Extraction Technique*.—In view of the various difficulties encountered when the solutions are turbid (whether by reason of bacterial slime formation or otherwise), for accurate results an extraction procedure was adopted which also had the advantage of being somewhat more sensitive.

For this purpose a known volume of the leachate was made up to 100 ml. with sea-water; 1 ml. of 20% ammonium citrate and 2 ml. of 3*N* ammonia were added, and then 5 ml. of the thiocarbamate reagent. When it had been allowed to stand for 15 min., the whole was transferred to a 250-ml. separating funnel and shaken for 1 min. with 10 ml. of chloroform. The chloroform extracts the yellow copper complex, and the heavier yellow layer, after being allowed to settle, was drawn off and estimated colorimetrically in a 1-cm. optical glass cell on the Spekker, the spectrum violet filter again being employed.

It is important in using this extraction method to make the final volumes of sea-water and of reagents identical for all the estimations and for the calibration of the instrument. Chloroform is soluble in sea-water and an appreciable amount of the copper complex remains in the "aqueous" layer, but, provided that the conditions of extraction and shaking are kept constant, this is immaterial; the calibration curve constructed under similar circumstances is strictly linear. Many investigators have recommended other solvents for the extraction, such as carbon tetrachloride, amyl alcohol, amyl acetate, &c. In these investigations none better than chloroform has been found and water-insoluble extractants such as CCl_4 have the additional disadvantage that very prolonged shaking or several successive extractions with small fractions of the solvent are required to remove all the copper from the aqueous layer.

The chloroform-copper solutions are stable for several hours and extracts can thus be accumulated for estimation at the end of a working day.

The greater sensitivity of the method arises from the fact that the copper colour from up to 100 ml. of leachate can all be concentrated into 10 ml. of chloroform; the extinction coefficient and consequent accuracy of estimation is correspondingly increased.

(d) *Estimation of Mercury*.

For the estimation of mercury, a solution containing 20 mg./litre of diphenyl thiocarbazon ("dithizone") in chloroform is used. If shaken with an aqueous mercury solution, a more dilute dithizone will give a positive colour change with an

amazingly small quantity of mercury, as little as one part in 200,000,000 being detectable in distilled water, provided that the solution is buffered and deoxygenated. Considerable difficulty was experienced in stabilizing the colour change in sea-water and in eliminating the interference of copper. The normal copper content of sea-water is high enough to give a strong colour with the dithizone reagent.

At a later date, to eliminate many of these difficulties, a modification of Hubbard's * method was tried, in which interference from copper and lead was eliminated by an involved series of treatments of the dithizone extract with sodium thiosulphate, acid permanganate, and hydroxylamine hydrochloride. The method, though perfectly workable, was cumbersome and unsuited to large numbers of determinations. One useful improvement followed on the work of Tompsett †: The dithizone was given a laboratory purification before use. The resulting colours were then much more reproducible and stable.

The method that has finally been adopted is as follows:

A.—*Preparation of the Dithizone Stock Solution*.—To 100 ml. of a chloroform solution containing 0.1 g. of commercial dithizone is added a similar quantity of 0.5% aqueous ammonia. This mixture is shaken for 1 min. and the chloroform layer is run off into a second separating funnel. A quantity of 5–10 ml. of pure chloroform is now added to the first funnel, shaken, and the chloroform washings are added to the second funnel. The second funnel is now shaken with 100 ml. of ammonia solution, the chloroform-dithizone layer is run into a third funnel, followed by a chloroform wash as before, and the whole process is carried out for a third time, at the completion of which the chloroform layer has changed from a deep green to a brick-red colour which is due to dithizone impurities; the chloroform layer is then discarded. A final wash with 5–10 ml. of chloroform is also discarded.

The three remaining aqueous ammoniacal fractions are filtered into a single large (1000-ml.) separating funnel; this fraction contains the purified dithizone. To this solution is added 100 ml. of pure chloroform and 20 ml. of an aqueous SO_2 solution.

The dithizone is precipitated, and on shaking is taken up into the chloroform layer. Additional SO_2 solution is added until all the dithizone is precipitated and transferred to the chloroform which is then withdrawn and kept as a stock solution under aqueous SO_2 .

For use, 2 ml. of this solution are made up to 100 ml. with chloroform.

B.—*Estimation Technique*.—To save time and

* D. M. Hubbard, 1940, *Industrial and Engineering Chemistry (Analytical Edition)*, 1940, vol. 12, p. 768.

† S. L. Tompsett and A. B. Anderson, *Biochemical Journal*, 1935, vol. 29, p. 1851.

to increase the amount of mercury to be determined, the "mercury portions" of 30 ml. from each of the three leaching slides of any given paint (leaching tests were always done in triplicate) are collected together in a 250-ml. separating funnel. An addition of 10 ml. of sea-water is made to bring the volume up to 100 ml. and after adding 2 ml. of 25% nitric acid the mixture is shaken for a few seconds. At this stage the contents may be left for 1-2 hr. if it is not convenient to carry out the colorimetry at that time. Otherwise 1 c.c. of 0.4% hydroxylamine hydrochloride is added and shaken up. The final stage is the addition of 5 ml. of the diluted dithizone reagent which is vigorously shaken for exactly 1 min.*

The coloured chloroform layer is run off into a 1-cm. cell and its absorption is measured immediately with a blue-green filter (4900 Å.). The Spekker can be used for this purpose with a "spectrum blue-green" filter, but at Millport a Zeiss Pulfrich visual photometer was generally used. Apart from the fact that the Zeiss 1-cm. cells can be used with only 4 ml. of solution (the standard Spekker cells required 8 ml.), the Pulfrich was used largely as a matter of convenience. A leaching test of 150 slides for copper and mercury (a standard day's work for the leaching team at Millport) required two colorimeters and kept four or five technicians occupied for most of the afternoon, the morning being spent in cleaning and rinsing glassware and setting up the test.

It is essential to determine the absorption of the chloroform layer immediately after shaking. The final colour is often stable only for a few minutes, especially in bright light. Subject to this qualification, the method will detect mercury at a leaching rate of 0.3 $\mu\text{g.}/\text{sq. cm.}/\text{day}$ in the presence of any normal copper leaching rate.

(ii) Effect of the Paint Constituents on Leaching Rate and Anti-Fouling Life.

The correlation between the copper leaching rate in the laboratory and the anti-fouling effectiveness in the sea has been clearly brought out in the earlier section of this report. The next step was to determine what factors in the composition controlled the rate of loss of poison and to correlate such results with further exposure tests.

These earlier leaching experiments were carried out on small (100-g.) batches of paints crudely milled in a small power-driven pestle and mortar mill. Such compositions were not ground in any sense of the word, all that was achieved being a more or less adequate mixing of the pigments with the varnish. All the leaching curves obtained

showed a high initial loss of copper (presumably due to cuprous oxide particles at the paint film surface which were unwetted by the varnish and thus freely dissolved in the early stages of soaking) which fell off to an approximately steady level (Fig. 8). "Milling" such compositions with aluminium stearate was found to diminish greatly this initial copper loss. Later paints (which form the subject of a separate paper) properly milled in a ball mill did not show this high initial loss of copper.

(It is understood that some commercial manufacturers do not mill their compositions but merely mix the pigment and vehicle in a vertical mixer;

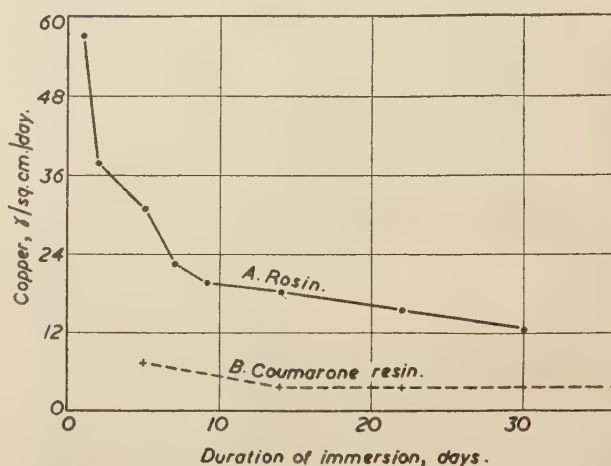


Fig. 8.—Leaching Rate of Copper from Two Poorly Dispersed Paints.

it is therefore not surprising that the leaching curves of some proprietary materials show the same characteristics of high initial copper loss. There is no evidence that any advantage is gained by such mixing, although the excessive copper loss in the first few days is very small in terms of the total copper content of the paint, so that there is also little disadvantage. On the other hand the physical qualities of the paint film should be improved by thorough milling.)

This early work was cut short by unforeseen circumstances and had to be abandoned. It seems worth while, therefore, merely to summarize the results which it suggested in a few brief paragraphs. The leaching rates below are all given in $\mu\text{g.}/\text{sq. cm.}/\text{day}$.

(a) Effect of Period of Immersion. (The Leaching-Time Curve.)

The effect of the period of immersion is shown in Fig. 8 and has been described above. In view of the rapid initial loss of copper, the results

* If slime formation was heavy, the chloroform formed an emulsion which only broke with difficulty after long standing. This problem could be overcome in most cases by the addition of 2 ml. of absolute alcohol immediately after addition of the hydroxylamine.

below (unless otherwise stated) have been calculated as an average of (usually) three determinations made at approximately 10, 20, and 30 days after immersion.

(b) *Effect of Pigment Wetting with Aluminium Stearate.*

The following figures indicate the effect of wetting with aluminium stearate:

Period of Immersion, days.	Leaching Rate.	
	With Stearate.	Without Stearate.
1	23.7	37.2
7	33.4	34.6
14	32.2	31.7
24	17.0	14.0

The lower initial value was followed by almost identical figures for the later part of the curve.

(c) *Effect of Cuprous Oxide Content.*

The relationship between the copper content and the leaching rate was as follows:

Copper content, %.	6	12	18	24	30
Leaching rate	7.7	12.7	16.5	21.1	25.4

This relationship was approximately linear above 6% of copper (present as cuprous oxide). At 6% the rate was rather higher than this linearity would suggest. As the inert extender was added in the form of red oxide to a constant total pigment weight, the oil absorption of the pigment fraction was appreciably changed by alterations in proportion of the two pigments. The control paint with no cuprous oxide was appreciably thicker in consistency than the cuprous oxide paints.

This result suggested that if the anti-fouling effect depends on the leaching rate of copper, then for every pigment-varnish system there is a single copper content which produces the maximum efficiency of the composition. A copper content less than this will fail to prevent fouling; more copper will be wasted, and the life of the paint will be approximately the same as for all (successful) paints. In an actual series of patches painted with these paints the lives (estimated by Mr. K. A. Pyefinch) proved to be as follows:

Copper content, %.	6*	12	18	24	30
Anti-fouling life, days	100	132	114	138	122

These figures are in good agreement with the above hypothesis.

(d) *Effect of Mercuric Oxide Content.*

The addition of mercuric oxide to a paint containing cuprous oxide considerably depressed

its rate of loss of copper, as shown by the following figures for six paints which all contained 24% of copper (as cuprous oxide) in the same varnish medium:

Mercury, %.	0	3	6	9	12	15
Leaching rate of copper	21.0	19.4	14.9	13.6	10.1	10.1

Quite apart, therefore, from the toxic effect of mercuric oxide, its presence should appreciably prolong the life of such an anti-fouling paint. This again was confirmed by the following observations (K.A.P.) on the life of a paint containing 6% of cuprous oxide:

Mercury, %	0	3	6	9	12
Life, days	100	138	178	198	225

(The evidence here is of course weak as the poisonous action of the mercury may add to the life of the composition. It has been previously noted that, in the presence of mercury, a copper leaching rate of 5-7 $\mu\text{g./sq. cm./day}$ (instead of 10) of copper has been found to indicate adequate anti-fouling properties in these paints.)

(e) *Effect of Content and Nature of Inert Pigment.*

This factor was not dealt with in the present series of experiments, but formed the subject of a later investigation described in a separate report.

(f) *Effect of the Varnish Medium.*

A.—*The Nature of the Resin Component.*†—This is the most important factor in the successful preparation of an anti-fouling composition. In the present series of tests the following variants were tried, using the same oil content and keeping all other experimental factors constant:

Resin Used.	Leaching Rate of Copper, $\mu\text{g./sq. cm./day}$.
Rosin	15.6
Ester gum	3.1
Acid rosin-modified phenolic	4.3
Esterified rosin-modified phenolic	1.9
Coumarone	3.8
Bitumen	1.7

Partial replacement of various amounts of rosin by ester gum gave the following corresponding leaching rates:

Ester-gum/ rosin, %	0	10	20	40	80	100
Leaching rate	18.7	12.2	4.8	3.4	2.9	3.1

Modification of the rosin with a reactive phenolic varied the leaching rate as follows:

Phenolic/rosin ratio, %	0	10	14	25	50
Leaching rate	18.2	4.3	4.3	3.8	3.8

* The leaching rate of 7.7 for this point was sufficient to prevent fouling by all but the most resistant organisms, and its life of 100 days can therefore be calculated on the same basis as those of the other paints in the series.

† All paints described in this section were milled with varnishes containing 100 g. of the resin component to 25 g. of leaded linseed-oil.

Partial replacement of rosin by miscellaneous other materials gave the following figures :

	Leaching Rate of Copper, $\mu\text{g./sq. cm./day.}$
(100% rosin)	(15.6)
30% paraffin wax	13.2
30% naphthalene	13.6
30% lanolin	3.6
10% coal-tar pitch	6.0

B.—*The Rosin/Oil Ratio*.—"Long-oil" varnishes gave appreciably lower leaching rates than "short-oil" varnishes, as is shown by the figures given below :

Oil/rosin ratio (weight)	0.25	1.00	2.00
Leaching rate	15.0	9.6	8.2

It is evident that the rate of loss of copper is a function of the rosin in the varnish, which is appreciably soluble in the slightly alkaline sea-water and enables the paint film to release its contained poison. An increase in the "insoluble" binder fraction, whether brought about by increasing the proportion of drying oil or by replacing the rosin by more stable and less hydrolysable synthetic resins or bitumens, reduces the copper leaching rate very considerably. The results show that the factors which govern slime formation on a non-toxic paint film closely parallel those determining the rate of loss of copper from cuprous oxide pigment in a similar film. They can readily be explained if both bacterial attack and copper loss are dependent upon the solution of rosin in the sea-water.

The results quoted above refer to a set of paints formulated under a specific set of constant experimental conditions. They show a number of properties of general interest, but it must not be assumed that such properties are characteristic of formulations based on the above but made up under different conditions, nor of formulations based on raw materials which may differ widely from those used here. It is believed, however, that such variations will not greatly affect the general principles set out above.

(iii) Practical Significance of a Laboratory Leaching Test.

Though the correlation between the laboratory leaching tests described above and the anti-fouling properties of the paint in a raft exposure test is satisfactory, a good deal of care is necessary in the interpretation of such a leaching test, as the following facts will show :

(a) The laboratory leaching rate is not usually constant under the conditions of storage and testing which have been employed. Fig. 9 shows a typical copper leaching curve obtained in this way. The paint should clearly be anti-fouling, since almost the whole of the leaching curve lies above the critical level of $10 \mu\text{g./sq. cm./day}$; this was confirmed in a panel-test exposure. But

the curve showed an initial (2-day) high loss of copper falling to a minimum at approximately 7 days after immersion, from which it rose to a new maximum between 30 and 60 days. After this it fell very slowly up to 240 days, when the test was discontinued.

(b) This variation in laboratory leaching rate makes it necessary to establish the portion of the curve which is of importance in assessing the anti-fouling performance. It was found that the plateau from 30-120 days gave the best basis for this prediction and in practice the average of the 30- and 60-day leaching figures has been employed for this purpose. (A test under 60 days would be

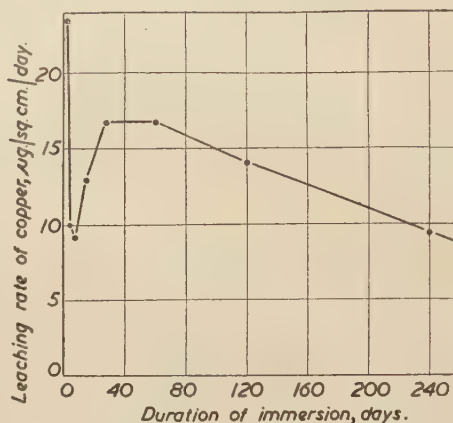


FIG. 9.—Leaching Rate of Copper from a Typical Formulated Anti-Fouling Composition.

quite possible if the experiment had to be shortened.)

(c) There still remains the problem of using the laboratory leaching test to predict the anti-fouling life of the paint. This will clearly depend on the copper reserve in the paint film as well as on its actual rate of loss on the ship or exposure panel in the sea. The difficulty in calculating this life in the present series of tests arises from the fact that, *between* leaching tests, the slides are stored in the very slowly flowing current in laboratory sea-water storage tanks. Owing to the fact (established by analysis of the total copper in the paint film) that copper loss during the storage in such sea-water tanks is less than that during the leaching test and is also less than the loss in the sea, it is obvious that the time-scale of the laboratory test is not equivalent to that of a sea exposure, *i.e.*, that, although individual leaching rates may be significant, the *integrated* leaching curve does not give the total copper loss.

The actual exposure life of the paint referred to in Fig. 9 was found to be only 100 days but the *laboratory* leaching curve is still above the critical level at 240 days.

(d) There is reason to believe, from estimates of the copper loss from paints continuously

immersed in the sea, that the laboratory leaching test outlined earlier gives a rough estimate of the rate of continuous loss of copper in such a marine immersion test, *i.e.*, that it can be used for an approximate prediction of the exposure-test life if the copper content is known. What is needed is a careful study of the relationship between the leaching technique and the chemical history of a marine paint exposure. It may also be pointed out that to predict the anti-fouling life of a composition on a ship, it is necessary to know the rate of loss of copper from a rapidly moving surface; there is reason to believe that it is considerably higher than that from a panel in a stationary raft exposure test. These problems are at present being followed up by Dr. H. Barnes, who will be publishing a separate account of this work. At the moment, it is sufficient to add that the obvious solution—the carrying out of leaching tests on slides “stored” in the sea—is difficult, though not impossible, in rather stormy waters with a very large tidal rise and fall as is the case at Millport. It is also necessary to keep in mind that inland laboratories may need to use the leaching technique (for which artificial sea-water is as serviceable as the natural variety) so that the development of a method which does not require continuous marine exposure of the test slides is of considerable practical value.

(3) THE USE OF ORGANIC POISONS IN ANTI-FOULING COMPOSITIONS.

It is well known that many organic compounds are toxic to plants and animals at extraordinarily low concentrations. A good deal of work has therefore been carried out to see if such materials could serve as the anti-fouling agent in suitable paints. It was to be expected that highly toxic compounds might be effective at far lower leaching rates than those of copper and, therefore, that in a suitably durable paint matrix they might provide an exceptionally long-lived anti-fouling coating.

The first step in this work was to choose suitable poisons for the experiments with the help of toxicity tests on various marine organisms. These tests were started by the author and Mrs. E. M. Harris at Millport in 1941. The early test animal used was, for technical reasons, not a fouling organism, but a small marine crustacean, *Har-pacticus fulvus*, which could be collected at all seasons of the year and successfully bred in the laboratory. (The use of this animal was suggested to us by Mr. R. Elmhirst, Director of the Millport Marine Biological Station, and he very kindly maintained the cultures required for these early studies.)

* The figures given for “toxicity” in this and later remarks are all calculated as the negative logarithm (to the base 10) of the concentration in gramme/millilitre required to produce a 50% mortality. Thus, a toxicity of 4 means that 50% of the animals are killed at a concentration of 10^{-4} or one part in 10,000 of the poison. A toxicity of 6 indicates a 50% kill at a concentration of one part per million, and so on.

At a later stage the work was taken over and considerably expanded by Dr. H. Barnes and Miss F. A. Stanbury at Plymouth. They used a different but very closely related crustacean, *Nitocra spinipes*, and they also developed special testing techniques applicable to red, green, and brown seaweeds.

Briefly, the techniques employed for these toxicity tests consist in estimating by interpolation the concentration of the poison in sea-water which kills 50% of a population of the test animal in 6 hr. For the red and brown seaweeds the decolourization produced in the healthy seaweed when it becomes moribund was used to indicate a predetermined standard of toxicity. A separate method had to be devised for the green seaweeds which do not become decolourized when poisoned. The falling off in their ability to synthesize starch by photosynthesis was estimated by iodine-staining a fragment (previously bleached in darkness) after exposure in daylight to the various concentrations of the poison.

The results of these tests on the animals are included in Table I.

It has been found in this work that several organic compounds and a number of metallic salts exist which are toxic to animals at one thousandth and to seaweeds at one hundredth of the lethal concentration of copper as copper sulphate. (The toxicity* of copper sulphate to animals is 4.6 and to seaweeds, 5.1-6.0.)

A second feature of the results is the *specificity* of many of the poisons employed. This is very marked in the organic derivatives and is illustrated by the following figures:

Substance.	Toxicity—	
	to Copepod — log conc.	to Plants Mean — log conc. for 3 species.
Pyrethrum (unstabilized) . . .	6.1	3.7
Pyrethrum (stabilized) . . .	7.0	4.0
p-Dimethylamino azobenzene . . .	8.0	2.7
Chlorphenarsazine . . .	8.0	3.0
Derris extract . . .	8.0	3.0
Tetraethyl thiuram monosulphide . . .	6.1	3.0
Nitroso resorcinol . . .	7.6	3.8
Aminoazotoluene . . .	6.6	2.7

Since many of the substances investigated were taken from the literature on insecticides, this characteristic is not surprising. In general, it would appear that while metallic poisons are highly toxic to both animals and plants, the organic compounds are relatively much less toxic to the seaweeds.

A detailed discussion of the chemical and biological implications of this work of Barnes and Stanbury would be beyond the scope of this report, but it is worth pointing out that two quite

TABLE I.—*Toxicity of Compounds in Sea-Water.*

The compounds were tested in solution in sea-water. The toxicity figure represents the negative logarithm of the concentration in grammes/millilitre needed to kill 50% of the animal population studied or to decolourize the red and brown seaweeds (*Lomentaria articulata* and *Laminaria digitata*). Toxicity to the green seaweed (*Enteromorpha intestinalis*) was estimated by the effect of the poison on starch photosynthesis.

Compound.	Toxicity to—			
	Animal (Crustacean).	Plant (Seaweed).		
		Red.	Brown.	Green.
Mercury thiocyanate	9.0	6.5	...	6
Mercuric chromate	8.6	7.5	7.5	7
Copper arsenate	8.4	6.0	7.5	7
Copper cyanide	8.4	6.5	7.5	6
Copper salicylate	8.4	7.5	7.5	7
Copper thiocyanate	8.4	...	7.5	7
Lead thiocyanate	8.4	...	6.5	7
Mercury ammonium chloride	8.4	7.5	7.5	7
Mercury salicylate	8.4	6
2 : 4-Di-isobutyl phenol	8.2
4-Nitroso- <i>o</i> -cresol	8.2	5
Nitroso- <i>m</i> -cresol	8.2	6.0	6.0	...
Amyl <i>m</i> -cresol	8.0	6.5	6.5	...
Ethyl bromoacetate	8.0
Chlorphenarsazine	8.0
Cobalt mercury thiocyanate	8.0	7.5	7.5	7
Di-(<i>p</i> -dimethylamino)-benzophenone	8.0	...	5.5	6
Phenyl mercury nitrate	8.0	6.0	5.5	...
Tetramethyl thiuram disulphide	8.0	...	5.5	5
Nitroso-resorcinol	7.6
Lead salicylate	7.5	6.0	7.5	7
Antimony oxalate	7.0	6
Cadmium oxalate	7.0	6.0	6.0	5
Pyrethrum (stabilized)	7.0	6
Trichlorophenol (Hg salt)	6.9	...	5.5	...
4-Nitroso-1-naphthol	6.8	6
Phenyl mercury acetate	6.7	5.5	5.5	5
Allyl isothiocyanate	6.6
Pentachlorophenol	6.2
Pyrethrum (unstabilized)	6.1	5
Derris extract	6.1
Aminoazo-toluene	6.0
<i>p</i> -Chlor- <i>m</i> -xylenol	6.0	6.0	6.0	6
Copper ethyl acetoacetate	6.0
Monochlor-isothymol	6.0	5
Monochlor-thymol	6.0	5.5	6.0	6
Pentachlorophenol (copper salt)	6.0	...	5.5	...
Pentachlorophenol (mercury salt)	6.0	...	6.0	...
Sodium arsenite	6.0
Tetraethyl thiuram monosulphide	6.0
Trichlorophenol	6.0
Zinc phenyl dithiocarbamate	6.0	4.5
Thiocyano benzthiazole	5.9	6
Trichlorophenol (Cu salt)	5.7	6
4-Chlor-2 : 6-dinitrophenol	5.6
Copper oxalate	5.6	7.0	7.0	7
Carbazole	5.4	...	6.5	...
<i>o</i> -Cresotic acid	5.4	5
<i>p</i> -Dichlorobenzene	5.4
Nicotine abietate	5.4	6
Phenothiazine	5.4	6
Tetraethyl thiuram disulphide	5.4	...	5.5	5
<i>n</i> -Methyl benzthiazole thione	5.3	5
MERCURIC CHLORIDE	5.22	6.6	6.2	4.5
Salicyl anilide	5.22	5
Benzthiazyl-2-methyl-sulphide	5.0
Chlorinated phenols	5.0	5
<i>m</i> -Dinitrobenzene	5.0
Diphenylamine	5.0
<i>o</i> -Nitroanisole	5.0	...	6.0	...
<i>o</i> -Nitrobenzyl cyanide	5.0
Resorcinol	5.0
4-Amino-1 : 2'-azonaphthalene	4.8
Phenoselenazine	4.8	5
Nitrosophenol	4.7	6
COPPER SULPHATE	4.6	5.1	5.3	6
Methyl dimethyl dithiocarbamate	6.5	6.5	4.5

TABLE II.—Tests on Anti-Fouling Coatings Containing Organic Poisons.

Ref. No.	Organic Poison.	Toxicity.	Naphtha Solubility.	Fouling on Organic Poison Coating.								
				In Rosin-Oil Paint.			In Rosin-Oil Paint with Cu ₂ O.			In Cementiferous Paint.		
	NONE (Control)	●	●	●	○	○	○	●	●	●
1	Phenyl arsonic acid	4.0-*	6	●	●	●	○	○	○	●	●	●
2	Ditto (sample from another source)	4.6	8	●	●	●	○	○	○	●	●	●
3	<i>o</i> -Nitrophenyl arsonic acid	4.0	6	●	●	●	○	○	○
4	<i>p</i> -Aminophenyl arsonic acid	4.0-	7	●	●	●	○	○	○	●	●	●
5	Phenyl arsenious oxide	4.7	5	●	●	●	○	○	○	○	○	○
6	Diphenyl arsenious oxide	5.8	4	○	○	○	○	○	○	○	○	○
7	Diphenyl arsenic acid	6.8	4	●	●	●	○	○	○	●	●	●
8	Copper diphenyl arsenate	4.0	7	●	●	●	○	○	○	○	○	○
9	β-Chlorovinyl arsenious oxide	5.0	7	○	○	○	○	○	○	●	●	●
10	ββ'-Dichlorovinyl arsenious oxide	5.8	2	●	●	●	○	○	○	●	●	...
11	Trichlorovinyl arsine	6.7	2	●	●	●	○	○	○	○	○	○
12	Chlorphenarsazine	8.0	6	○	○	○	○	○	○	○	○	○
13	10-Ethyl-5:10-dihydrophenarsazine	5.0	2	○	○	○	○	○	○	○	○	○
14	Arsenobenzene	5.0	5	●	●	○	○	○	○	○	○	○
15	Zinc isopropyl xanthate	5.5	6	●	●	●
16	Ferric dimethyl dithiocarbamate	6.0	6	○	○	○	○	○	○	○	○	○
17	(i) Zinc phenyl dithiocarbamate	6.0	8	○	○	○	○	○	○	○	○	○
18	(i) <i>iso</i> Propyl phenyl carbamate	5.0	2	●	●	●	○	○	○	○	○	○
19	(i) Methyl dimethyl dithiocarbamate	4.0	1	●	●	●	○	○	○	●	●	●
20	Diphenyl thiourea	5.5	6	●	●	○	○	○	○	○	○	○
21	Di- <i>o</i> -tolyl thiourea	6.0	3	●	●	●	○	○	○	●	●	●
22	Tetramethyl thiuram monosulphide	6.0	4	○	○	○	○	○	○	○	○	○
23	Tetramethyl thiuram disulphide	8.0?	2	○	○	○	○	○	○	○	○	○
24	(i) Tetraethyl thiuram monosulphide	6.0	3	○	○	○	○	○	○	○	○	○
25	Tetraethyl thiuram disulphide	5.4	1	○	○	○
26	(m) Aniline disulphide	5.3	1	○	○	○	○	○	...	○	○	○
27	(i) Thiocyno benzthiazole	5.9	3	●	●	●	○	○	○	●	●	●
28	(i) <i>N</i> -Methyl benzthiazole thione	5.3	2	●	●	●	○	○	○	●	●	●
30	Phenothiazine	5.4	2	●	●	●	○	○	○	●	●	●
31	Selenodiphenylamine	4.7	6	○	○	○	○	○	○	○	○	○
32	Phenoxtellurine	4.0	...	●	○	○
33	Diphenylamine	5.0	1	●	○	●	●	●
34	Fluorene	...	1	●	○	○	○	○
35	Fluorenone	...	1	○	○	○
36	Carbazole	5.4	2	●	●	●	○	○	○	○	○	○
37	Acridine	6.6	3	●	●	●	○	○	○	●	●	●
38	<i>p</i> -Dichlorobenzene	5.4	2	●	●	●	○	○	○	●	●	●
39	<i>p</i> -Iodonitrobenzene	5.0	2	○	○	○	○	○	○	●	●	●
40	Benzyl chloride	...	1	●	●	●	○	○	○
41	<i>m</i> -Dinitrobenzene	5.0	1	●	●	●
42	Chloronaphthalene (mixed)	5.3	1	●	●	●	○	○	○	○	○	○
43	α-Nitronaphthalene	4.5	1	○	○	○	○	○	○	●	●	●
44	<i>p</i> -Amino acetanilide	4.0-	3	●	●	●	○	○	○
45	<i>p</i> -Chloro acetanilide	4.0	3	●	●	●	○	○	○	●	●	●
46	<i>p</i> -Bromo acetanilide	4.6	6	●	●	●	○	○	○
47	(i) Salicyl anilide	5.2	5	○	○	○
48	Sulphanilamide	4.0-	8	○	○	○	○	○	○	○	○	○
49	Benzoquinone	...	6	○	○	○
50	<i>o</i> -Nitroanisole	5.0	1	●	●	●	○	○	○	●	●	●
51	Pentachlorophenol	6.2	1	●	●	●	○	○	○
52	2:4:6-Trichlorophenol	6.0	1	●	●	●	○	○	○
53	2:4:5-Trichlorophenol	4.6	1	●	●	●	○	○	○
54	2:4-Di- <i>isobutyl</i> phenol	8.2	1	●	●	●	○	○	○	●	●	●
55	4-Chloro-2:6-dinitrophenol	5.6	1	●	●	●	○	○	○	○	○	○
56	<i>p</i> -Chlor- <i>m</i> -xylene	6.0	2	●	●	●	○	○	○	●	●	●
57	Monochlor-thymol	6.0	1	●	●	●	○	○	○	●	●	●
58	Monochlor- <i>isothymol</i>	6.0	1	○	○	○	○	○	○
59	Pentachlorophenol (copper salt)	6.0	5	○	○	○	○	○	○
60	Pentachlorophenol (mercury salt)	6.0	4	○	○	○	○	○	○
61	Pentachlorophenol (copper pyridine complex)	6.8	4	○	○	○	○	○	○
62	Aminoazo-toluene	6.0	1	●	●	●	●	●	●	●	●	●
63	(i) 4-Amino-1:2-azonaphthalene	4.8	1	●	●	●	●	●	●	●	●	●
64	(i) <i>p</i> -Dimethylamino azobenzene	4.0-	1	●	○	○	○	○	○	○	○	○

* The minus sign invariably follows a value of 4.0 and is inserted to indicate that the median lethal effect was observed at a concentration greater than 10⁻⁴.

TABLE II.—Continued.

Ref. No.	Organic Poison.	Toxicity.	Naphtha Solubility.	Fouling on Organic Poison Coating.								
				In Rosin-Oil Paint.			In Rosin-Oil Paint with Cu ₂ O.			In Cementiferous Paint.		
	NONE (Control)	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
65	(i) Benzene azonaphthol	4.0-	1	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
66	(i) Ditto (copper complex)	5.7	5	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
67	(i) o-Hydroxy-benzene azonaphthol	5.0	4	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
68	(i) Ditto (copper complex)	4.0-	4	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
69	(i) Di- <i>p</i> -dimethylamino-benzophenone	8.0	2	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
70	(i) <i>p</i> -Nitroso dimethyl aniline	5.8	1	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
71	(i) <i>p</i> -Dimethylaminophenyl thiocyanate	6.2	1	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
72	(i) <i>p</i> -Dimethylaminophenyl isothiocyanate	7	3	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
73	<i>p</i> -Nitrobenzyl cyanide	5.0	2	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
74	(i) Dodecyl thiocyanate	5.5	1	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
75	Nitro- <i>m</i> -cresol	8.2	5	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
76	4-Nitroso- <i>o</i> -cresol	8.2	4	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
77	Nitrosophenol	4.7	5	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
78	4-Nitroso-1-naphthol	6.8	5	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●
79	(i) Phenyl methyl nitrosamine	5.5 ?	1	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
80	<i>o</i> -Cresotic acid	5.4	4	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
81	<i>m</i> -Cresotic acid	...	5	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
82	Ethyl bromoacetate	8.0	1	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
83	(i) <i>N-N</i> -Amyl benzyl cyclohexylamine	5.5	1	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
84	Quinoline	6.0	1	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
85	Acriflavine	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
86	Malachite green	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
87	Pyrethrum (stabilized)	7.0	1	● ● ●	○ ○ ○	● ● ●	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●
88	Derris extract	6.1	2	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
89	Nicotine abietate	5.4	(2)	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	● ● ●	● ● ●	● ● ●
90	Phenyl mercury acetate	6.7	8	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○	○ ○ ○
91	Phenyl mercury nitrate	8.0	6	○ ○ ○	○ ○ ○	○ ○ ○
92	Phenyl mercury phthalate	● ● ●	● ● ●	...	○ ○ ○	○ ○ ○
93	Phenyl mercury stearate	● ● ●	● ● ●	...	○ ○ ○	○ ○ ○
94	Phenyl mercury linoleate	● ● ●	● ● ●	...	○ ○ ○	○ ○ ○
95	Phenyl mercury naphthenate	○ ○ ○	● ● ●	...	○ ○ ○	○ ○ ○
96	Naphthyl mercury acetate	○ ○ ○	● ● ●	...	○ ○ ○	○ ○ ○

Ref. No.—The reference numbers are arbitrary. The compounds marked (i) were suggested by I.C.I., Ltd., and those marked (m) by Messrs. Monsanto Chemical Corporation, Ltd.

Toxicity.—The figure given is the negative logarithm of the median lethal concentration in grammes per millilitre; e.g., 4.0 means that 1 g. in 10⁴ ml. kills 50% of the test organisms.

Naphtha Solubility.—An arbitrary figure ranging from very soluble (1) in naphtha to insoluble (8).

Fouling Records.—The groups of three circles represent fouling at approximately 6, 12, and 18 weeks after immersion. The state of fouling is compared with that on a non-poisonous control panel at the same date.

○ Negligible fouling.

○ Slightly fouled.

● Moderately fouled.

● Heavily fouled.

distinct factors may be concerned in the poisoning of an organism living in a toxic solution: (i) The quantity of poison in the body which is required to kill it, and (ii) the rate of penetration of the poison through the body surface. If the organism can excrete the poison, the effective rate of penetration is of course reduced by the amount which is eliminated in this manner. It is known that the rate of penetration of ions into living cells is very much lower than that of un-ionized compounds and that fat soluble materials penetrate relatively quickly. It is found that the poisonous action of copper and mercury on the crustacean may be greatly enhanced when these metals are present as salts of organic acids and that this enhancement also occurs in many results on the seaweeds. That the acid radical is not directly

responsible for the enhanced toxicity is shown by the low toxicity of its sodium and potassium salts.

During the years 1942 and 1943 extensive small-scale panel tests were carried out at Millport with some 250 paints containing organic poisons both alone and in combination with cuprous oxide. Table II. summarizes the results of the largest series of experiments which are described below.

The anti-fouling coatings used for this series of tests were made up in three forms for each organic poison tested:

(a) A rosin coal-tar-pitch/linseed-oil varnish medium, milled with 50% of bauxite residue red and 10% of organic poison (calculated on the wet weight of paint).

(b) The same varnish medium with 40% of

bauxite residue red, 10% of organic poison, and 10% of Cu_2O .

(c) A cementiferous coating containing about 30% *by volume* of the organic poison (the weight of organic poison varied from 10 to 20% of the pigment, depending on its specific gravity).

The results on cementiferous coatings will be described later; for the present, attention will be confined to those on oil-resin paints (a) and (b).

The rosin/pitch/oil combination is not a good anti-fouling varnish but its use in earlier tests (*see* the First Report of the Marine Corrosion Sub-Committee (*loc. cit.*)) enabled the present results to be correlated with those on earlier paints containing combinations of Cu_2O and HgO . A combination of 12% of Cu_2O with 4% of HgO in this medium had shown an anti-fouling life in panel tests of 6-9 months and it was considered, if the organic poison could be used effectively in a normal paint medium, that the present test should give at least a useful indication of the fact.

The exposure tests could not be continued as long as was desired because the protective undercoat that was used proved to be unsatisfactory. Assessments of fouling were, however, carried out at 6, 12, and 19 weeks after immersion as shown in Table II. Exposures were carried out in duplicate (in some cases in triplicate) for each paint. Several control areas, some containing bauxite residue red only, and others 50% of bauxite residue red with 10% of Cu_2O were included with every set of panels immersed.

The fouling records are calculated by adding the separate ratings for grass, hydroid, and shell (each ranked into the eight categories 0-7, where 7 represents a complete covering of the organism). For ease of interpretation the results are shown in the form of shaded circles which represent the density of fouling when compared with that on a non-toxic control panel.

It is immediately clear that many of the most poisonous compounds have little or no anti-fouling effect; *e.g.*, the phenols (Nos. 51-58, Table II.) which (apart from No. 53) are highly toxic to the test animal are without exception complete failures in the anti-fouling compositions. Only the copper salt of pentachlorophenol, No. 59, shows any appreciable anti-fouling effect and it has been found by leaching experiments that this effect is probably little more than can be accounted for on the basis of its copper production.

The compounds which do possess appreciable anti-fouling properties are:

(1) Several organic arsenicals, *e.g.*, diphenyl arsenious oxide, β -chlorovinyl arsenious oxide,

chlorphenarsazine, and 10-ethyl 5:10/dihydrophenarsazine.

(2) Several derivatives of thiocarbamic acid, *e.g.*, ferric dimethyl dithiocarbamate and zinc phenyl dithiocarbamate.

(3) Closely related to the above, derivatives of thiourea, *e.g.*, a few thiuram sulphides, though none of these is outstanding.

(4) Ethyl bromoacetate (a tear-gas).

(5) Derris extract.

(6) Phenyl-mercury compounds.

All these organic poisons have a relatively high toxicity to the test organisms but, as they represent only a few of the highly toxic compounds studied, it is interesting to consider why these are successful, while others, equally toxic, are failures. Barnes and Stanbury have carried out a good deal of painstaking work on this subject. By using certain organic dyestuffs milled into paints they were able to determine the rate of loss of such dyestuffs into water when the paint surface was immersed.

For a dyestuff (methylene blue) that is very soluble in water but insoluble in the paint constituents, a "leaching curve" (which was obtained by rotating a cylindrical painted specimen in distilled water and measuring the accumulation of the dye in the water bath) showed an enormous initial loss of dye—as much as 30% being eliminated in the first 9 days. After this, there was a steady rate of loss of methylene blue to the water, averaging 9.4 $\mu\text{g.}/\text{sq. cm.}/\text{day}$, *irrespective of the initial dye concentration in the paint*. The initial "wastage" of dye was approximately proportional to the initial dye content if this was greater than 10%. For dye contents of 10% or less, the relative wastage was much lower.

Examination of the paint surface soon after immersion showed that the dyestuff was leaching out of minute pores in the paint; the high wastage of dyestuff is thus supposed to be due to the washing out of these pores which may have been produced by the poor milling technique.

With cuprous oxide paints in the same medium and with the same milling, the author has shown that the wastage of copper was of the same order for a 10% paint and that the final rate was also similar. A striking difference, however, was that in the Cu_2O paint, when the final leaching rate was approximately proportional to the Cu_2O content—in sharp contrast to the results with methylene blue. The high wastage in both cases is probably related to the milling technique as the end-runner or "pestle and mortar" type mill gave very poor dispersion.*

The initial loss of dye for a methylene-blue

* The fact that the methylene blue paint was leached into distilled water, while the cuprous oxide curve was obtained with sea-water, vitiates a too detailed comparison of the results which, however, probably provide a guide to the freely exposed particles of pigment (responsible for "wastage") in both cases.

paint was decreased by prolonging the drying time; this result is directly opposite to that obtained for cuprous oxide paints, where long drying time increased the initial leaching rate of copper; the final leaching rate after 2-3 weeks was unaffected in both cases.

The similarity in form of the leaching curve for methylene blue and copper in these paints is doubtless related to the fact that both "pigments" are insoluble in the paint medium but are readily leached out by water. The very high (1200 $\mu\text{g./sq. cm./day}$) initial rate of loss of methylene blue is to be expected from its high water solubility. (The fact that the final leaching rate is independent of the initial methylene-blue

wastage, naphtha-soluble organics are very likely to affect the film properties, and Barnes and Stanbury have shown that in the case of pentachlorophenol (and probably with dinitrophenol also) the film produced imbibes water very much more freely than the normal paint film. The two factors together will lead to a rapid exhaustion of the paint containing a naphtha-soluble poison and the later low rate of loss of poison may also be explained as a type of partition effect between the paint gel and the sea-water.

The above very brief summary does scant justice to Barnes' and Stanbury's very careful work, but it suffices to point out that organic "pigments" which are highly naphtha-soluble

TABLE III.—*Relationship between Fouling Toxicity, and Naphtha Solubility for Organic Poisons in Rosin-Oil Paint.*

		Toxicity of Poison.					
		3.0-3.9.	4.0-4.9.	5.0-5.9.	6.0-6.9.	7.0-7.9.	8.0.
Naphtha Solubility.	Soluble, 1-2.	● ○	● ● ● ●	● ● ● ● ● ● ● ● ● ● ● ● ● ● ● ● ● ●	● ● ● ● ● ● ● ● ○ ● ● ● ○	●	○ ● ● ○ (A)
	Fairly soluble, 3-4.	● ●	●	● ● ● ○	● ● ● ● ● ● ● ● ○	● (A)	● (A)
	Slightly soluble, 5-6.	●	● ● ● ● ● ●	● ● ●	○ ○ ○ (A)	(A)	● (A)
	Very slightly soluble or insoluble, 7-8.	● ●	● ●	○ (A)	○ ● ○ (A)	(A)	(A)

Explanation.

The signs in the table refer to the fouling assessments after 12 weeks on the organic poison paint in the rosin-oil varnish without cuprous oxide.

Toxicity and solubility indices are those from Table II.

With few exceptions the compounds which have any appreciable anti-fouling effect are found in the lower right-hand corner of the table, the sections concerned being marked (A).

content is somewhat surprising; the diffusion coefficient of the dye molecules (much less than that of the Cu'' ion) may be limiting the rate of loss.)

A second coloured organic compound investigated by Barnes and Stanbury gave very different leaching results. Dinitrophenol is a brilliant yellow in colour, fairly readily soluble in naphtha (about 6 g./100 g.) but not very soluble in water (about 0.05 g./100 g.). A paint made with 10% by weight of dinitrophenol gave an even higher initial rate of loss than that of methylene blue; the leaching rate fell off continuously down to the extremely low value of 1.9 $\mu\text{g./sq. cm./day}$ after an immersion lasting for 13 days.

A material with a high naphtha solubility will be deposited on the surface of the paint film by the evaporating solvent in the paint; this film of the organic poison can be clearly seen in many cases (e.g., with paints containing di(*p*-dimethylamino) benzophenone). In addition to this source of

can be expected to show rapid exhaustion and very low ultimate leaching rates for anti-fouling paints which contain them. It was therefore of interest to compare the performances of the various organic poison paints with (a) the toxicity test values and (b) the naphtha solubility, for each compound.

The results are summarized in Table III., where the amount of fouling developed in 12 weeks is entered in a correlation diagram whose rows and columns give the naphtha solubility and the toxicity (to marine crustacea), respectively.

The solubility in naphtha was graded for this purpose into four categories: Very soluble, soluble, slightly soluble, very slightly soluble or insoluble.

It is seen that low fouling values (successful anti-fouling action) occur nearly always in the lower right-hand region of the diagram. This means that in order to be successful an organic

poison must be toxic to copepods at a concentration of 10^{-5} (or less) and be relatively poorly soluble in naphtha. These are not the only requirements and some compounds fulfilling them do show poor anti-fouling properties, but they are almost a *sine qua non*.

The result of adding cuprous oxide to an anti-fouling composition containing organic poison is often anomalous. The toxic action of the cuprous oxide is frequently reduced by this process since the organic compound may, by its action on the paint matrix, reduce the copper leaching rate below the value normal for such a cuprous oxide paint. Trichlorovinyl arsine (No. 11, Table II.) has this effect. After 3 months' immersion the control cuprous oxide paint had a copper leaching rate of 6.5 $\mu\text{g./sq. cm./day}$, while the cuprous-oxide/organic-poison paint had a copper leaching rate of only 3.0. Other cases of organic poisons having a similar effect on the cuprous oxide paint are probably found in Nos. 79, 83, 84, and 87 (Table II.). The last-named (No. 87, pyrethrum) was supplied dissolved in a heavy mineral oil and it is presumed that the mineral oil was the factor concerned in the reduction of the leaching rate of copper.

The Leaching of Organic Poisons from Paints.

It is clearly of interest to determine the rate of loss from paints into sea-water of some of the organic poisons which were found to be effective anti-fouling agents. Unfortunately most of the substances are difficult to estimate in such minute quantities as those produced by the leaching test. Dr. H. Barnes has, however, succeeded in estimating the poison leaching from a paint containing chlorphenarsazine (*DM*, the well-known sternutator used in chemical warfare) by a method based on the production of an intense pink colour when the compound is oxidized with hot, strong nitric acid, then made alkaline, and taken up into aqueous acetone.

The method will be described in detail by Dr. Barnes in a later communication in which the results will also be dealt with, together with a more detailed presentation of much of the work on organic poisons.

IV.—Experiments on Cementiferous Anti-Fouling Compositions.

The cementiferous paints dealt with in this section were originally developed, entirely for anti-corrosive purposes, by Dr. U. R. Evans and his colleagues at Cambridge. It is no function of this report to describe these paints in detail; they are characterized by a dry pigment fraction containing metallic zinc which is mixed with a special aqueous vehicle immediately before applica-

tion. The paint thus produced is of a normal consistency and can be applied in the usual way with a brush (or striker). Within a short time (about 30 min.) it sets to a spongy mass, later hardening to a cement-like coating which adheres very powerfully to the steel basis.

Up to September 1944, when the author left Millport, a large number of marine exposure tests on these coatings were carried out for Dr. Evans. In the course of these tests it was found possible to incorporate organic poisons into the pigment fraction of the cementiferous paint without adversely affecting its protective properties and so the possibility of using these paints as anti-fouling compositions was actively explored. Most of the earlier experiments were done on a cementiferous system, described as *E412*, which was applied in two coats, only the top coat containing an organic anti-fouling agent. It was found later that the poison could be successfully incorporated into the undercoat and the possibility of a one- or two-coat system which was both protective and anti-fouling has since been studied in raft tests and in patch tests on vessels in service. The results of anti-fouling tests on cementiferous coatings containing organic poisons are included in Table II.

Advantages of Cementiferous Coatings.

The advantages of cementiferous coatings may be summarized as follows:

(a) The coatings can be applied with considerable success to wet rusty steel partially covered with adherent mill scale. (Loose mill scale is removed by wire-brushing.)

The Millport two-coat systems (in which only the top coat incorporated an organic poison) described in Table II. were carried out in duplicate patches on pickled and weathered specimens 24×24 in. in size. In no case was any breakdown of the coating or any appreciable rusting observed up to 12 months, after which the panels were removed as all but two of the test-patches were heavily fouled. The weathered plates possessed about 20-40% intact mill scale and were substantially coated with adherent rust.

(b) As they are "water paints" they can be applied under very adverse weather conditions.

In one experiment, where painting was being carried out in the open air, a heavy rainstorm broke while painting was in progress. This did not interfere with the painting and the coating showed no signs of premature breakdown on exposure. A damp atmosphere has no deleterious effect and considerable amounts of water on the steel surface are merely incorporated into the coating without adverse effect.

(c) Their adhesion to the steel is remarkable. Nothing short of pickling the panel will remove

the coating E412 from steel after some months of immersion in sea-water.

(d) They are more successful in withstanding mechanical damage than are oleoresinous coatings as an area from which the paint has been abraded does not spread by flaking and/or under-rusting.

(e) They possess a considerable power of protection at "holidays," i.e., a scratch line through to the bare metal corrodes only to a small extent or not at all.

On one or two occasions gales have been responsible for severe scraping of the test-plates by detached adjacent specimens. Such heavy scoring of the coating has never spread to wider areas of breakdown and a small amount of initial rusting is all that can usually be seen. The huge "warts" of rust found over unpainted areas surrounded by (most) oil paints have never been seen on this cementiferous coating.

(f) It seems possible (though further evidence is needed on this point) that they may continue to function successfully after drying out and re-immersing in sea-water.

Specimens sent to Dr. Evans for inspection after exposure have on occasion been returned and re-immersed for periods of up to 6 months without harm. Taken in conjunction with the use of organic anti-fouling agents, this suggests the important possibility of being able to dry-dock a ship several times without re-coating, except perhaps for a limited amount of "touching-up."

(g) The presence of many organic poisons does not interfere with the protective properties of the coating.

(h) From a practical point of view it is worth pointing out that ordinary commercial anti-fouling compositions can easily be applied over cementiferous undercoats. The anti-fouling coating "keys" very well into the porous substratum and often has a much longer life than it does over its own oleoresinous protective. For example, a series of thin plates cut from tinplate steel (which is very difficult to protect with oil paints as rusting spreads from the edges) were coated with various cementiferous protectives, painted over with one coat of a proprietary anti-fouling, and immersed for 10 months at Millport. Several of these showed no rusting or fouling in this period (though occasional slight flaking of the anti-fouling coating occurred) but controls painted with the complete proprietary system failed catastrophically in this period, showing up to 60% of rusted surface and being completely covered with mussels.

These advantages may be summarized in a single statement, viz., that it seems possible that cementiferous coatings may permit of the application on to wet, rusty steel, partially covered with mill scale, of a single coat having both protective

and anti-fouling properties, which are not affected by drying out and re-immersion.

The "non-toxic" control patches of coating E412 applied to the panels appear to have a slight anti-fouling effect. The corresponding oleoresinous paints containing organic and organic-plus-copper poisons were immersed at the beginning of March, whereas the cementiferous paints were not put out until about a month later; consequently the fouling on the cementiferous paints should have been appreciably greater than on the comparable oleoresinous systems.

This toxicity is probably provided by the zinc ions diffusing out from the cementiferous coating. Chemical tests have shown that the leaching of zinc from such a coating into sea-water—at least in the early life of a cementiferous coat—is very rapid indeed and probably quite sufficient to exert an anti-fouling effect in spite of the low toxicity of zinc ions. (The rate of loss of zinc is of the order of twenty times the minimum effective loss of copper from a copper anti-fouling paint.)

In one or two of the cases shown in Table II., organic poisons appear to increase the fouling on these cementiferous coatings. This only occurs in the early stages (the first 6 weeks) and it is interesting to note that compounds Nos. 1, 2, and 4 (with heavy anti-fouling ratings at 6 weeks) are all acids. Presumably in the presence of these acids the discharge of toxic zinc ions may be greatly reduced.

An interesting point was observed in connection with the *attachment* of fouling to cementiferous coatings. On most of the test-patches the few barnacles which settled never succeeded in establishing a firm attachment to the coating although they grew to a considerable size. Very slight mechanical force dislodged them completely without leaving a calcareous base attached to the substratum. This fact, coupled with the very few barnacles which were found on the cementiferous coatings, suggests that at normal ship cruising speeds barnacles may not persist on these surfaces.

It would be unfair to present such a favourable picture of these paints without pointing out some of their present disadvantages. These may be listed as follows :

(a) Though they dry quickly (1-2 hr.) they are rather sensitive to mechanical damage for a short time after painting and can even be washed off the plate by a heavy water flow (e.g., from a scupper discharge) if this occurs within a few minutes of painting.

(b) Coating E412 does not protect well under atmospheric conditions; i.e., the steel should be immersed within a reasonably short interval (a few days) after painting.

A plate coated with a single undercoat of E412

was left for 3-4 weeks before the application of the second (anti-fouling) coating. During this time extensive rusting in the form of minute rust spots had taken place over the whole surface which consequently had to have a second protective coat before immersion. It has already been noted that, *once immersed*, subsequent drying of the coating has no such deleterious effect.

(c) The coats require a little care in application. The mixture of pigment and vehicle sets after about 30 min. in air and it is necessary to apply the coating within roughly 15-20 min. of mixing. Some organic anti-fouling agents greatly accelerate this setting process and make the combination useless for practical purposes.

As the mixing process is not a difficult one—it is no more troublesome than mixing whitewash, nothing but simple stirring being required—it is only necessary to see that the correct proportion of pigment to vehicle is used. At the correct consistency the paint is very easy to apply as it does not “drag” the brush and, being an aqueous suspension, flows into all pits in the steel with ease. Although it is therefore only possible to mix sufficient paint for 15-20-min. work, the speed of covering a surface is slightly higher than with most oil paints so that it is probable that the inclusive rate of painting would be as high for cementiferous as for normal oleoresinous coatings.

(d) Up to the present time, cementiferous coats have been tested with only fairly high poison concentrations, amounting to 10-25% by weight of the (wet) coating. As none of the effective organic poisons is cheap, the material would be expensive to use. Experiments are now in progress to determine how far the amount of poison may be reduced while still retaining anti-fouling properties. It is noteworthy that if a single coating can be made to serve the purpose of the three-coat system of the oil paint, a much more expensive coating becomes a practicable proposition as it economizes in material and, even more important, in time and labour.

(e) The surface of the finished coating is rough

and may show an appreciable skin-friction increase as compared with an ordinary paint surface. This point requires investigation.

Since the cementiferous coating has the properties of a porous inorganic cement, a long anti-fouling life will require the use of an organic poison which is very slightly water-soluble and which gives a reasonably “flat” leaching curve of the poison into the sea-water. Once the general type of poison has been decided upon, the leaching requirements may be more easily met for cementiferous than for oleoresinous coatings, which require adjustment of the poison with respect to both water and naphtha solubility to achieve success. The control of water solubility alone can often be achieved by the alteration of some chemical radical or side chain without greatly changing the toxicity (*e.g.*, in phenyl-mercury compounds by changing the acid radical).

Acknowledgments.

The frequent references in the text to the work of various colleagues will, it is hoped, provide an indication of the extent to which the author is indebted to them for much of the material on which this report is based.

Grateful acknowledgment is made to the Members of the Marine Corrosion Sub-Committee who individually and collectively have assisted actively in this work; in particular, the enthusiasm and untiring help of the late Dr. G. D. Bengough, F.R.S., as Chairman of the Sub-Committee, demand a special tribute. His loss was as serious a blow as that of Dr. W. H. Hatfield, F.R.S., to whom the work owes its inception.

The author is particularly and personally indebted to Mr. R. Elmhirst, Director of the Scottish Marine Biological Station, and to his staff, for the provision of facilities and secretarial assistance, and for unofficial help at all times and in all weathers!



FIG. 4.—Fouling after approximately Three Months' Exposure on Slides Coated with 27 Experimental Anti-Fouling Compositions. Each group of six slides comprised two formulations made with the same varnish; the four vertical slides were coated with cuprous oxide as the only toxic pigment and the two horizontal slides with mercuric oxide and cuprous oxide pigments. The copper leaching rates of the cuprous oxide paints were as follows :

(6) 6.2	(7) 5.4	(8) 3.2	(9) 5.9	(10) 4.2	(11) 5.9	(12) 4.0	(13) 4.0
(14) 2.0	(15) 2.6	(16) 3.5	(17) 2.6	(19) 10.3	(18) ...		

The heavy fouling on two of the four slides painted with varnish (6) is due to mechanical breakdown of the paint film, which has exposed the glass surface to fouling; on the two slides with intact paint the fouling is very light. The 108 slides were arranged at random over the whole carrier so that the intensity of fouling was variable. The four slides painted with varnish (18), with cuprous oxide as the only poison, lost the entire paint film through flaking.

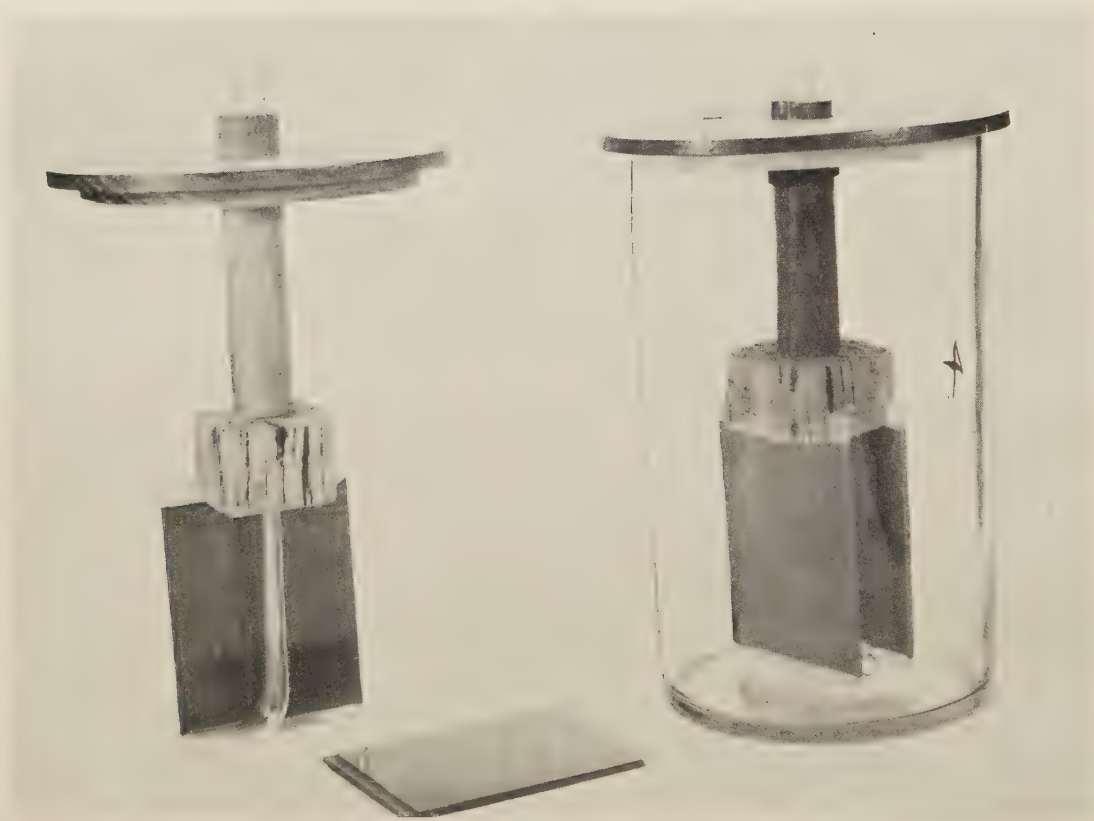


FIG. 1.—Photograph of Leaching Apparatus.

[Leaching-Rate Test Panel.

[To face p. 335 P.

INTERIM DESCRIPTIVE STATEMENT ON THE LEACHING-RATE TEST FOR SHIPS' ANTI-FOULING COMPOSITIONS.*

BY THE JOINT TECHNICAL PANEL ON THE LEACHING-RATE TEST OF THE MARINE CORROSION SUB-COMMITTEE.†

(Fig. 2 = Plate XLIV.)

Paper No. 19/1946 of the Corrosion Committee (submitted by the Panel on the Leaching Rate Test, through the Marine Corrosion Sub-Committee).

SYNOPSIS.

This preliminary statement on the leaching-rate test for anti-fouling paints has been prepared in response to a demand from a section of the paint trade and is the result of work by investigators attached to the Marine Corrosion Sub-Committee of The Iron and Steel Institute and the British Iron and Steel Research Association, and by their collaborators on the Admiralty Corrosion Committee.

The test is designed to assess the value of anti-fouling compositions by measuring the rate of loss of toxic ingredients from the paint surface during immersion in sea-water. Originally developed in the U.S.A. for application to anti-fouling compositions containing cuprous oxide as the only toxic ingredient, the test is being adapted for use on formulations containing more than one toxic constituent and in particular on those with copper and mercury, to which type most of the British proprietary compositions belong.

In conducting the test, small glass panels coated with the anti-fouling compositions under test are stored in sea-water and transferred periodically into the leaching apparatus, where they are subjected to agitation (by bubbling) in a definite amount of sea-water for a standard time; the toxic substances leached into the water are then determined. It is essential that the ratio :

$$\frac{\text{Paint area} \times \text{Test duration}}{\text{Volume of sea-water used for leaching}}$$

is kept constant. The determination by colorimetric methods (using a "Spekker" photo-electric absorptiometer) of the small amounts of copper and mercury leached into the sea-water is described.

In the simplest case of anti-fouling compositions containing cuprous oxide only, it is known that a steady loss of copper of about 10 microgrammes/sq. cm./day is effective in preventing fouling. This is termed the "critical leaching rate" for copper. The critical rates for mercury, for copper and mercury in the same composition, and for other anti-fouling poisons are not yet sufficiently defined for statement, although it is known that the rate for mercury is less than half of that for copper.

The statement emphasizes that, at present, exact standardization of the test has not been achieved, nor has its precise significance in relation to service behaviour been fully determined. Further work on points requiring elucidation is being carried out in several laboratories.

I.—INTRODUCTION.

THE Marine Corrosion Sub-Committee of The Iron and Steel Institute and the British Iron and Steel Research Association have had under consideration the desirability of publishing data which their investigators, together with collaborators on the Admiralty Corrosion Committee, have accumulated concerning the leaching-rate test for evaluating anti-fouling compositions. Moreover, there has been a demand for such a statement from the

section of the paint trade concerned, in order that the interests both of manufacturers and users might be promoted. For this purpose the Sub-Committee set up a Panel, the terms of reference of which included the investigation, standardization, and significance of the leaching-rate test on anti-fouling compositions. The following were appointed to this Panel :

Dr. H. Barnes.
Dr. E. N. Dodd.
Mr. L. Kenworthy (*Secretary*).

* Received January 30, 1946.

† A Sub-Committee of the Joint Corrosion Committee of The Iron and Steel Institute and the British Iron and Steel Research Association.

Mr. J. C. Kingcome.
 Mr. B. L. Luscombe.
 Dr. I. G. Slater (*Convenor*).
 Dr. H. G. Stubbings.

The attainment of the objectives mentioned, however, has proved to be a far from simple matter. Many points still require elucidation even as regards the technique of the test itself; moreover the precise significance of the test as a method of assessing the performance of anti-fouling compositions is still largely unknown. Consequently, it should be realized that the statement herewith presented is essentially of an interim nature, although it is hoped that it will serve a useful purpose both for immediate needs and future developments.

The leaching-rate test, which originated in the U.S.A.,* is a measurement of the leaching rate or loss of toxic ingredient from a paint film immersed in sea-water and is expressed in microgrammes ($\mu\text{g.}$) of toxic ingredient liberated from 1 sq. cm. of paint surface per day ($\mu\text{g./sq. cm./day}$). The leaching rate (of a poison from a paint containing a single poisonous compound such as cuprous oxide) above which all major types of fouling organisms are prevented from settling and developing has been designated the "critical leaching rate" of the poison. In the case of copper and mercury compounds this is expressed in terms of the metallic radical. It should be noted here that although two main types of toxic ingredients are considered in this statement (*viz.*, cuprous and mercuric oxides), most of the work carried out on the problem to date, both in the U.S.A. and in this country, has been confined to anti-fouling paints containing copper (as cuprous oxide) as the only toxic constituent.

Investigations on anti-fouling paints containing cuprous oxide as the only toxic constituent have indicated that the critical leaching-rate value is of the order of 10 $\mu\text{g.}$ of copper/sq. cm./day, under conditions of sea storage. The critical leaching rate for mercury, in the absence of copper, is known to be less than that for copper alone and, unlike copper, appears to vary with the medium. Further evidence on this point is being pursued.

It is appreciated, however, that copper and mercury compounds are used together in many anti-fouling compositions; no reliable data yet exists regarding the critical values involved in these instances. The behaviour and efficiency of the metals in the presence of each other are not simple additive functions of the amounts of each present and of their relative toxicities, and are not yet fully elucidated. Less still is known of the effect of other poisonous ingredients. Investi-

gations of the leaching rate of various organic poisons are in progress.

II.—APPARATUS AND TECHNIQUE FOR CARRYING OUT THE LEACHING-RATE TEST.

In carrying out the test, ground-glass plates are brush coated with the anti-fouling composition under test, allowed to dry for a given period of time, and are then stored in sea-water, from which they are removed periodically for estimation of the leaching rate. Storage can be conducted in the sea or in a laboratory tank. If the latter is used, the water should be renewed frequently enough to prevent the copper content of the water reaching a value at which the rate of further dissolution of copper from the paint is restricted. This value is thought to be well below 0.5 mg./litre (0.5 $\mu\text{g./ml.}$). Up to the present, most of this experimental work has been carried out with natural sea-water. Synthetic sea-water has, however, been proved equally satisfactory when standardized, and is clearly more convenient where inland laboratories are concerned.

It should also be pointed out that the leaching rates obtained with sea storage and tank storage are not identical, probably owing to variations in external conditions, the chief of which appear to be the degree of agitation and the temperature. For this reason it is thought that the ultimate method should comprise a standardized tank storage.

Experimental work so far conducted has indicated that the ratio:

$$\frac{\text{Area of paint under test} \times \text{Duration of test}}{\text{Volume of sea-water used for leaching}}$$

is a critical consideration. Earlier experiments, including the American work,¹ have suggested that this ratio should approximate to 60 min./cm., but more recent experiments have suggested that for certain types of paint this value may require considerable modification. For example, during the actual leaching test on certain paints, the rate of increase in the concentration of copper in the leachate is not constant. Nevertheless in the experiments so far carried out the value of 60 min./cm. has been used. A description of a suitable apparatus is given below.

The leaching apparatus is shown in Figs. 1 and 2 and consists of a cylindrical glass vessel with a close-fitting wooden lid through which passes a central wooden supporting tube carrying a glass tube of approximately 8 mm. bore. At one side of the lid a vent-hole is provided. The lower end of the glass tube is bent at right-angles at a point 2.5 cm. from the end of the tube. The distance from the top of the supporting tube to the lid is

* This test was independently developed by the Sub-Committee in the early days of its work, but no claim for priority is made on this account, since the recently published work of the American investigators¹ anticipated that of the Sub-Committee by several years.

about 2.0 cm. but this distance is not fixed, in order to allow for slight variation in size from jar to jar. The glass tube likewise projects about 2 cm. above the wooden supporting tube, to permit the attachment of rubber tubing.

The external diameter of the lower 3 cm. of the wooden tube is thinned down to 1.5 cm., and this portion carries a shellac-impregnated cork which is grooved on the lower side to carry the two painted plates; the dimensions and general arrangement are shown in Fig. 2.

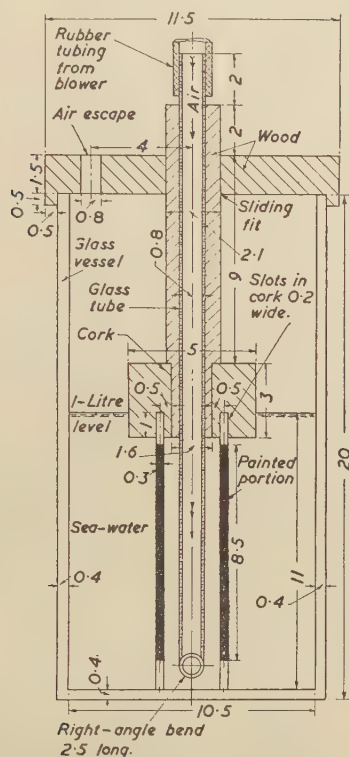


FIG. 2.—Leaching Apparatus. (All dimensions in cm.)

The apparatus is designed to take two ground-glass plates of $11 \times 7 \times 0.3$ cm.; the side edges of the plates are bevelled off to reduce the likelihood of fracture of the paint film. The painted area of each plate (which includes the side edges) is fixed at 125 sq. cm. and, with the above dimensions, the length of plate painted equally on both sides is 8.5 cm.; slight modification of these linear measurements may be necessary to give the required area. The plates as specified are just covered by one litre of sea-water when in position in the leaching jar. This area of paint (250 sq. cm), leached in one litre of sea-water for 4 hr., gives the desired ratio (area \times time/volume = 60 min./cm.). Provided that this ratio is maintained, slight modifications in the dimensions of the apparatus are permissible.

The leaching conditions must be kept constant as to paint area, volume of sea-water, and duration of leaching. The temperature of the leaching

units must be kept constant at 25° C. in a bath, and the physical properties of the sea-water should be relatively constant and approximately those of off-shore sea-water. Thus, the pH value should be about 8.0 to 8.2 and the chlorinity not less than 17 parts per thousand. (The pH value of sea-water taken into the laboratory has shown a tendency to drop slightly in a few hours, but the drop is not of serious dimensions.)

The water in the leaching jars is agitated by passing a steady stream of air through the glass tube at an approximate rate of 150 litres/hr. from a suitable blower. It is convenient to have a simple flow-meter in the air-line to each jar or series of jars, so that the requisite air flow can be adjusted quickly.

III.—PAINTING AND MANIPULATION OF LEACHING PLATES.

Well-stirred paint is applied by a soft $\frac{1}{2}$ -in. brush to plates which have previously been tared. At least three pairs of plates should be used for any one test (giving results in triplicate) and each plate should carry approximately the same weight of paint (roughly of the order of 0.01 to 0.02 g./sq. cm.). Painted plates should be allowed to dry in a horizontal position to avoid the formation of "tears". The duration of the drying time should be kept constant for a particular series of trials, as variations will influence the initial leaching rate of the paint. Different types of paint may require longer or shorter times of drying but, as a general guide, a drying time of 6 hr. has been found to be suitable for a large variety of compositions.

The dry weight of paint applied to each plate is recorded at the end of the drying period. In addition, it is an advantage, in correlating leaching rate with performance, to record the thickness of dry film; this may be calculated from the specific gravities of the mixed paint and the volatile solvent and the percentage content of volatile matter. Immediately after weighing, the dry plates are placed in holders and immersed in the sea or, if this is not possible, in tanks of running sea-water. The method of storage is important, as very different results will be obtained—especially during the early stages of leaching—from, say, plates kept in static tanks of sea-water and others kept in a tide-way. It is equally important to treat the surface of the paint with care. Plates should not be allowed to dry when being removed from storage to the leaching bath.

The surface must not be cleaned of detritus or slime immediately before leaching; such a procedure is liable to increase the leaching rate very considerably, especially during the early stages of leaching. On the other hand, the presence of this slime, which may be quite

thick (e.g., on paints containing rosin) may cause a false low leaching rate to be obtained; moreover, slime interferes with the analytical determinations. A compromise method has been adopted whereby the film is very gently brushed off several days before the plates are due to be leached. For this purpose, the plates are brought in and immersed overnight in sea-water to which approximately 1% of formaldehyde has been added, thus killing the bacterial slime, which is then removed by means of a soft brush. The plates can then be returned to sea-water storage until ready for leaching, as it takes some time for slime to re-develop. The pH value of formaldehyde-treated sea-water should be adjusted to that of the untreated water by the addition of alkali. Slime can be removed without treatment with formaldehyde, but the latter probably "sterilizes" the paint surface to some extent so that little slime develops in storage between the time of treatment and leaching.

Under service conditions the paint surface is continually bathed in fresh sea-water, whereas in the leaching apparatus the concentration of leached poison is accumulating steadily. If no agitation is provided, a layer of sea-water saturated with the poison forms at the paint surface and further leaching-out of the poison can only occur by diffusion from this saturated area. If the leaching rate is low, gentle bubbling will remove this saturated layer but, with higher leaching rates more violent bubbling, and even mechanical stirring, is necessary. For general purposes, and in the apparatus described, the bubbling rate already mentioned should suffice.

American workers have stated¹ that a copper concentration of 0.5 mg./litre ($\mu\text{g.}/\text{ml.}$) will in some cases restrict the rate of leaching. In the absence of further information it would seem desirable to avoid the accumulation of copper above this concentration.

IV.—INTERVAL BETWEEN LEACHINGS.

It is inadvisable to leach the same plates at close time-intervals, as the action of leaching affects the rate of loss of pigment and this must be given time to settle down again. An interval of one week is considered ample to eliminate errors from this source. If more frequent leachings are desired, e.g., during the early stages of exposure, then it is necessary to have several sets of replicate plates which can be leached in succession and then discarded or kept over the necessary time to return to normal.

V.—THE ESTIMATION OF COPPER AND MERCURY IN THE LEACHATE.

The determination of copper and mercury in leachates is carried out by colorimetric methods

using a photo-electric colorimeter, e.g., the "Spekker" photo-electric absorptiometer. Descriptions of this instrument and of its use are given in papers by Vaughan^{2,3} and Haywood and Wood.⁴

(a) *Estimation of Copper.*

A calibration curve, plotting "Spekker" drum readings against copper concentration (in mg./litre) is made by using 50-ml. samples of sea-water containing varying amounts of standard copper solution of known strength. The initial standard solutions of copper sulphate should be made up in distilled water, and only the final dilution in sea-water. In estimating leachates, lesser quantities may be taken, depending on the concentration of copper present, the volume being made up to 50 ml. with sea-water and the appropriate dilution factor used to correct the figure derived from the calibration curve or table. By adding a little sodium diethyldithiocarbamate solution to some of the leachate and observing the colour developed, it is possible, after a little experience, to judge the dilution required before proceeding to the quantitative determination.

In carrying out this estimation of copper, the following technique is adopted :

To 50 ml. of leachate (or diluted leachate) in a separating funnel are added in sequence—with shaking after each addition—10 ml. of 20% citric acid, 10 ml. of approximately 6N ammonia solution, and 2 ml. of 0.1% aqueous solution of sodium diethyldithiocarbamate. A period of at least 15 min. is allowed for the yellow colour of the copper complex to develop fully.

The copper complex is extracted with at least three lots of 10 ml. of carbon tetrachloride and the volume made up to 50 ml. The solution is run into the "Spekker" colorimeter cell and the drum reading taken, using Ilford "Spectrum Violet No. 601" filters.

A blank extraction on 50 ml. of the same sea-water as used in the leaching jars is carried out at the same time and the instrument set at a pre-determined drum reading on this. It is desirable with the "Spekker" colorimeter to use the drum range 0.400 to 0, as this part of the scale is more easily read.

(b) *Estimation of Mercury.*

Mercury is determined by a mixed colour method using diphenylthiocarbazone (dithizone) in chloroform solution.

In estimating mercury in leachates by extraction with dithizone, the amount to be determined lies very near the limit of quantitative accuracy; the difference in transmittancy of the chloroform extracts is small and near the limit of accuracy of the "Spekker" colorimeter. Accordingly all the precautions usual in microchemical analysis must

be most carefully adhered to if concordant results are to be obtained.

The thorough cleansing of the apparatus after every separation is emphasized. If this is done by soaking with dichromate/sulphuric-acid mixture this must be very thoroughly washed out before re-use of the apparatus. It has been found more convenient to use diluted dithizone for the purpose, as no unwanted chemicals are thereby introduced. Used separating funnels are washed out twice with sea-water and then with about 10 ml. of diluted dithizone solution immediately after use. Any mercury or copper adsorbed on to the glass is thus removed. Separating funnels are again rinsed with a few millilitres of dithizone before re-use, if they have been standing more than an hour or so. The use of chloroform/dithizone for this purpose is more expensive but is repaid in the great saving of time which would otherwise be required for cleaning the apparatus.

A.R. chloroform only is recommended for mercury estimations. If recovered chloroform has to be used, Biddle's method⁵ of purification is to be preferred.

Preliminary purification of the dithizone as purchased is necessary to remove oxidation products. Purification is carried out as follows: 0.1 g. of dithizone dissolved in 100 ml. of chloroform (A.R.) is extracted six times with 100-ml. portions of 0.5% ammonia solution. The dithizone passes into the ammoniacal phase and is then orange in colour. The pink oxidation products remain in the chloroform layer which is discarded. The combined ammoniacal extracts are washed with two 20-ml. portions of chloroform in a litre separating funnel, the chloroform layer being discarded. The dithizone is now reprecipitated from the ammoniacal solution by careful addition of sulphurous acid and redissolved in 100 ml. of chloroform.

This stock solution must be kept in the dark and at a temperature of less than 40° F., as it fades gradually; it must be further diluted 50 times immediately before use.

Because of the instability of dithizone in the light it is preferable to carry out dithizone extractions in a dim light and, if possible, to take the actual readings in a dark room or cubicle. The extracted solution should be read immediately it has settled sufficiently after shaking to be run off.

In view of the instability of the reagent and the possibility of the setting of the instrument varying, a saving of time can be effected if the instrument is set against pure chloroform, blank readings being taken before reading the unknowns; at least two blank extractions are advisable to guard against error. Using the dithizone solution as prepared above, a useful setting on pure chloroform is 0.700, when extracted blanks will give a reading of between 0.450 and 0.400, depending on the strength of the dithizone solution.

In carrying out the estimation, 2 ml. of 25% nitric acid, 1 ml. of 4% hydroxylamine hydrochloride solution, and 5 ml. of a freshly prepared 10% aqueous solution of potassium cobalticyanide are added (in this order) to 100 ml. of the leachate contained in a 250-ml. separating funnel, which is shaken after each addition. The mixture is allowed to stand for 10 min. and is then shaken briskly for 1 min. with 10 ml. of diluted dithizone solution. The dithizone layer is drawn off through a pad of filter paper into a 1-cm. "Spekker" cell and the drum reading taken, using Ilford "Spectrum Blue-Green 603" filters.

VI.—FURTHER DEVELOPMENTS.

Additional to the numerous points already mentioned, which are still undergoing investigation, accelerated methods of leaching are being examined whereby the effective leaching life of a paint is compressed into a short period for test purposes.

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Discussion on THE PROTECTION OF IRON AND STEEL AGAINST MARINE CORROSION AND FOULING.

The following three papers were discussed jointly: "The Formulation of Anti-Corrosive Compositions for Ships' Bottoms and Underwater Service on Steel.—Part II.", by F. Fancutt and J. C. Hudson; "Report on Anti-Fouling Research, 1942-44," by Professor J. E. Harris; and "Interim Descriptive Statement on the Leaching-Rate Test for Ships' Anti-Fouling Compositions," by the Joint Technical Panel on the Leaching Rate Test of the Marine Corrosion Sub-Committee.

JOINT DISCUSSION.

Dr. F. WORMWELL (Chemical Research Laboratory, Department of Scientific and Industrial Research, Teddington): I greatly value the privilege of opening the discussion on these three interesting and important papers, and I should like to say that the observations which I propose to offer constitute a joint contribution from Dr. W. H. J. Vernon and myself. Dr. Vernon greatly regrets his inability to be present.

The papers present a striking contrast in type and in the method of approach to the problems. I believe, however, that this is not fortuitous; indeed it arises from the state of knowledge of the subjects when the investigations were commenced. In the field of corrosion and paint technology, investigations into the mechanism of corrosion and the formulation of anti-corrosive paints have been proceeding in many countries for several decades, providing a good basis of information and working knowledge on which to build. In the case of fouling, however, although a good deal of work had been carried out on the problem, there was little accessible information based on systematic investigations. It was therefore necessary to institute fundamental research on fouling organisms. The Marine Corrosion Sub-Committee's investigators, led at first by Professor Harris and more recently by Mr. Pyefinch, have undoubtedly advanced our knowledge of the nature and habits of fouling organisms and their relative susceptibilities to various poisons.

Dealing first with the anti-fouling report, my colleague Mr. Butlin has raised the question whether there is any evidence of a causal relation between the onset of fouling and the initiation of corrosion, or *vice versa*. Possibly the attachment of organisms may create conditions suitable for the growth, for example, of sulphate-reducing bacteria, which may then stimulate the corrosion of the underlying steel. Mr. Butlin is now examining samples collected by Mr. Pyefinch and

Mr. Bishop of deposits from ships, but the evidence at present is insufficient to warrant definite conclusions. As for the converse question, whether the initiation of corrosion encourages fouling, it is clear that if there is sufficient corrosion to dislodge part of the paint, then anti-fouling efficiency will be impaired.

Dealing with the paper by Mr. Fancutt and Dr. Hudson, we should like to offer our sincere congratulations to the authors, as we do to Professor Harris and the authors of the paper on the Leaching-Rate Test, on their most interesting and valuable contribution. No doubt there are many aspects on which individual differences of opinion may arise, and there is scope for criticism on points of detail, but on the whole I think that the investigation can be described as a well-conceived, ably executed and systematic onslaught on the problem of formulating anti-corrosive paints for underwater service on steel.

Our own work at the Chemical Research Laboratory has been mainly concerned with laboratory corrosion tests, and more recently with accelerated tests intended to give information on the relative behaviour of protective coatings in specific types of service environment. Our experience has served to confirm our earlier views on the need for well-planned field tests such as those carried out by the present authors, not only to correlate with service conditions but to assess the value of laboratory tests.

With regard to the main conclusions in the Synopsis of the paper, we can heartily endorse the statement on the value of paint No. 173 and of suitable chlorinated-rubber paints. Accelerated tests with the C.R.L. high-speed rotor apparatus * at Teddington confirm the good quality of paint No. 173 in regard to adhesion and freedom from serious flaking and blistering under conditions of rapidly moving, well-aerated sea-water. Indeed, the resistance of this paint is such that laboratory

* G. D. Bengough, F. Wormwell, V. A. Yardley, and T. J. Nurse, British Patent No. 569,342.

tests of a still greater degree of acceleration will be necessary if the period of test is to be reduced below fifty days.

Although we have not tested the particular chlorinated-rubber paints formulated by the authors, our experience on other paints of this type indicates that outstanding performance in sea-water can be obtained by suitable formulations in this medium.

It is noteworthy that the authors decided to neglect deterioration at the edges of the specimen in assessing the results. Do they consider that this affects the relative ratings of the different paint systems? It is conceivable that paints offering greater resistance to breakdown at edges and corners—a valuable property in service conditions—may be placed at an undue disadvantage.

At the beginning of Section C of the paper there is a reference to the effect of film thickness on paint behaviour. On the basis of our own tests, we have found that, within limits, film thickness is not always a determining factor in comparing the relative merits of paints of *widely different types*. On the other hand, the authors have established (Fig. 4) a general correlation between the thickness and protective behaviour of paints of a given series. The superior performance of paints on pickled and weathered, as compared with as-rolled and weathered, specimens confirms earlier work. We agree that good results are not always obtained in sea-water immersion conditions when paint is applied to a *freshly* descaled surface. The authors rightly emphasize the marked contrast with the behaviour under atmospheric conditions, and this affords another illustration of the danger in corrosion work of extrapolating from one set of conditions to another.

We endorse the authors' view that comparative tests of different paints are best carried out on specimens descaled before weathering, although the performance of paints applied to as-rolled and weathered steel is of great importance in actual service conditions, for example, in the Mercantile Marine.

The authors are to be congratulated on their ingenious method of presenting the results. The visual summary in Fig. 6 is most helpful in giving a "bird's-eye view" of the relative behaviour of different media. In connection with the behaviour of 100% phenolic-resin media, we have observed in high-speed rotor tests that paints based on such media are generally intrinsically resistant, but they are susceptible to sudden loss of adhesion under conditions of rapid movement in sea-water. With regard to the use of paint No. 32 as a primer for new steel, our experience with accelerated tests confirms the authors' conclusions.

Finally, we can heartily endorse the authors' views on the great importance of carrying out as

many practical tests as possible on actual ships' bottoms.

Mr. D. H. HEWITT (Messrs. Lewis Berger and Sons, Ltd., London): I propose to confine my remarks to the paper by Mr. Fancutt and Dr. Hudson as it is in this paper that the paint technologist is particularly interested at the moment. Unfortunately the other papers did not reach me in time for study, but it is clear from a first reading that the biological and practical anti-fouling work are shaping in a very interesting way, and that paint technologists will be very much concerned with the new report which Professor Harris has promised us.

I should like to endorse everything that Dr. Wormwell said about the thoroughness with which the work recorded in the former paper has been tackled. A given field has been well investigated, and the results presented with a wealth of detail. Turning to specific points, from the point of view of paint technology, the interaction of pigment and binder is of primary importance, and something has been done in this paper to cover the weight and volume relationship of those two essential ingredients of the final film as formed. The authors have presented the work that they have done on that point with commendable caution, and point out that, in the particular series which they have chosen, they have used as their master paint one in which the properties are as good as might be expected, but it is possible not so much in this series as in the series to come, when the authors will deal with the preparation of paints for steelwork already painted, that this relationship will be of particular importance, because it has to do with the practical conditions under which performance is assessed. The carefully selected and prepared surfaces on which they have worked are the only possible surfaces on which they could have compared their variables, but under practical conditions of the application of marine compositions such surfaces are rarely available, and it is a fact that the average surface for repainting is extremely porous, and that porosity upsets the pigment/binder ratio very considerably.

Another aspect is connected with the use of the particular anti-fouling composition which the authors chose for use over their priming composition. Unfortunately its performance was not such as to allow tests to continue as far as they might have done, and it would be interesting to know what figure that paint gave on the leaching-rate test.

This raises the question of the importance eventually of joining together the work on anti-corrosion and anti-fouling compositions. It is obvious that it is necessary to approach the protection problem from two directions, but it is

also obvious that these two lines of attack will meet, and it is within the experience of many of us that the performance of a given anti-fouling composition is very largely determined by the anti-corrosion composition used beneath it. The two, in other words, must be assessed in conjunction. The reason for that, I think, is that there is mutual interaction between the two systems during the drying period, and also subsequently on ageing.

That brings me to one omission from this paper. It concerns the question of practical tests of the more successful compositions on new tonnage of which some of us had hoped for some record. There is a hint, I think, that such tests have been carried out, and in view of the very excellent results given on the raft test it would be most interesting to know what the experience has been with priming composition, particularly when used on new tonnage. It may well be that the compositions named in this paper have not received full service trials, but the assessment of those mentioned in the previous paper may by now have led to some information being available.

Dr. J. E. O. MAYNE (Cambridge University): My comments will be concerned with the paper by Mr. Fancutt and Dr. Hudson, but first I should like to congratulate all the authors on their excellent papers, and particularly on the very clear and concise manner in which they are arranged.

It may be that the outstanding results which have been obtained with chlorinated rubber are due to the fact that of all the media used it was the only one which yielded a film which was completely unsaponifiable. All the other media contained litho or linseed oil. With regard to the materials used in the preparation of the media, chlorinated rubber, Cereclor, and coumerone resins are unsaponifiable; phenol-formaldehyde condensation products are saponified with difficulty, whereas the remaining ingredients can be saponified with comparative ease.

If the total merit figures for the different vehicles given in the last column of Table VII. are arranged in decreasing order, they will be roughly in the inverse order of their relative ease of saponification. Sea-water is slightly alkaline. The conclusion which emerges, therefore, is that in the formulation of paints for the protection of steel against sea-water, the nature of the pigment is not so important as that of the vehicle, and the best vehicle is simply the one which has the maximum chemical resistance to sea-water.

Mr. W. A. D. FORBES (The Admiralty): It is quite impossible to scan these three papers as a whole without realizing that an enormous amount of work has been put into this attempt to solve the fouling problem. Moreover, it is evident from the quality of the papers, which is very high, that the

work has been carried out by a band of enthusiasts who have put their whole heart and soul into the solution of the problems confronting them. When this Institute considered the First Report of the Marine Corrosion Sub-Committee it was beginning to be realized that as poisons are put into anti-fouling paints to do a job of work, the way in which those poisons emerged was a matter worthy of study; and so we find in this second report that prominence is given to the question of leaching and to the correlation of copper leaching rates and degree of fouling. This is the first time, I think, that a series of copper-leaching-rate curves of anti-fouling paints has been put forward in a publication in this country.

I find, however, that the evidence for the correlation presented in the paper is far from convincing. In saying this I do not want to give the impression that I do not believe that the relationship between the copper leaching rate and fouling exists; on the contrary, I am convinced that it does. I feel, however, that after this lapse of time we ought to have a much more rigorous treatment of this fundamental proposition. If you glance at the curves given in the paper—which, after all, are only thumb-nail sketches and show just three points on each of the curves—you will realize that an error in any of the ordinates might lead to a considerable change in the character of the curves. The curves given in the third row of Fig. 5 are those for slightly fouled paints, but the first one must be heading for disaster after a period of only 120 days, as the leaching rate is falling very rapidly. The next two have very rapidly rising leaching rates. Presumably they started low, and the first spot on the curve is after 30 days, so that in practice it is quite likely that it would be found that, in an unfavourable environment, those two particular paints would have fouled long before their leaching rate had risen to a figure which would make them effective. These, of course, are proprietary paints, and so it will be realized how important it is that this correlation between leaching and fouling should be thoroughly established, and more satisfying evidence presented.

Since this correlation has come so much to the fore, it is quite obvious that some standardized method of carrying out leaching-rate tests is necessary, and here the work which has been done by Dr. Slater and his team is, I think, most valuable. Considerable difficulty, I understand, was found in harmonizing the views of the small circle of people concerned; and to my mind this in itself shows how important it is that a standardized method should be available in order that workers in other fields may compare their results. When a manufacturer comes to me and says "I have a very good anti-fouling paint; will you try it out?" the first thing I want to know is whether

there is a reasonable chance of it proving successful, because it is a very expensive matter thoroughly to try out anti-fouling paints. To my mind, the best guide to enable me to decide whether it is worth while even conducting panel exposures is to have a look at the shape of the copper-leaching-rate curve, if the paint contains copper as a main poison.

Some two years or so ago, the Admiralty initiated a series of trials of proprietary anti-fouling compositions, and we invited the manufacturers to supply as much information as possible about their paints, including the leaching-rate curves; but we found that only one manufacturer out of about thirty was prepared to produce this information, and quite a number of them asked what were the particular methods by which these leaching-rate characteristic curves were derived. If that is the general state of affairs in the industry, it is obvious that a need exists for a standardized method of measuring leaching rates.

The lamina theory put forward in this second Report of the Marine Corrosion Sub-Committee is very attractive, but needs consideration from various angles. It may well be that the existence of such a lamina is a real blessing, in that it may be the reason why anti-fouling paints applied to ships survive for long periods. But for this laminar layer the poisons might all be washed out in the course of a few weeks during a voyage, and the paint rendered ineffective. Not much is known about the actual laminar layer associated with ships in motion, except possibly by a few people who specialize in these problems. A good deal is known about the turbulent layer or frictional belt which accompanies ships in motion, but the laminar layer has not assumed for ships the importance it has for aircraft. It is the object of an aircraft designer to provide a shape of wing section which permits the air-flow to remain laminar over as great an area as possible. It is found that the air-flow will remain laminar so long as it is accelerating, but when it passes beyond that point turbulence sets in and there is a great increase in resistance. In the case of aircraft, even some dust falling on the wings will be sufficient to cause breakdown of the laminar layer, but when we come to deal with ships we are dealing with very much bigger objects than the wings of an aircraft, and it may well be that a much larger obstruction is necessary to cause a breakdown of the laminar flow, particularly as you go towards the stern of the vessel. I think there is little doubt that at the bow any degree of roughness is harmful in that it will cause a breakdown of the laminar layer, but as you go along the ship it is probable that a much larger projection is needed to cause a breakdown. It seems evident, however, that we must expect, and in fact we know that we get, greater turbulence at the after-

end of a ship than elsewhere. It follows, therefore, that if the lamina theory of the action of anti-fouling paints advanced by Professor Harris is correct, we might expect to find a more rapid rate of loss of poison at the after-end of a ship and an earlier breakdown of the useful life of the anti-fouling paint in this neighbourhood. Further, we should expect to find that the degree of fouling at the after-ends of ships would in general be greater than at the bows. I believe that that agrees with observations on actual ships, and lends support to Professor Harris' theory.

Taking this second report as a whole, I fear it gives little guidance to the formulators of anti-fouling paints. It would be difficult to determine for instance from this report whether the type of matrix to be aimed at should be the soluble type, which enables a new surface containing cuprous oxide to be continually presented to the fouling organisms, or whether an insoluble matrix with a very heavy loading of poisons to give poison particles in continuous contact—sometimes known as a cannon-ball effect—is the more desirable type of matrix for anti-fouling paints. My own preference lies with the soluble type as with this type the surface is always ready to meet the fouling attack immediately a ship returns to port. With the insoluble type of matrix it seems to me there may be grave danger, when a ship has been steaming at sea at high speeds and for long periods, that the surface of the paint on immediate return to harbour may be completely exhausted of poisons and require a considerable period for it to be again in a position to resist fouling, so that fouling may get a hold before the paint surface can recover and be in a position to meet the attack.

This aspect of the question leads me to suggest that the time is now ripe to initiate an advance in the technique of carrying out panel exposures. The panel test as now conducted is a static test and does not really represent the conditions obtaining on the surface of a ship which is at sea for the greater part of its life. To get a surface comparable to that presented by a ship returning to harbour from a voyage, we ought to attach our panels to a whirling arm, or something of that sort, where they could be subjected to the effects of motion at, say, 20 knots, for a fortnight, or something of that order, and then expose them on the raft in the normal way. This is not a novel suggestion; it has been made before, and it may be of interest to say that quite by chance I happened to notice in the minutes of the first meeting of the Marine Corrosion Sub-Committee, that Professor Harris attended, held as far back as January 1941, that this was one of the suggestions which he put forward at that meeting.

I should like to turn now to the paper by Mr. Fancutt and Dr. Hudson. I fully endorse all the remarks which have been made by other speakers

as to the value of the work done. It is unquestionable that here something of great value has been achieved, and the Marine Corrosion Subcommittee, and particularly the authors of this paper, have done a very fine piece of work and deserve congratulations. I should like to mention that the Admiralty has tried out paint No. 173 on a very large scale, and has found it very satisfactory indeed. Shipowners need have no fears in specifying a protective paint of this type. I note that the authors hope further to improve this paint, and I shall follow their attempts to do so with much interest. I am sure that when the work which they are doing in co-operation with the Association of Ships' Composition Manufacturers comes to fruition, we shall have completely satisfactory protective paints, particularly if the troubles associated with application under adverse weather conditions can be satisfactorily overcome.

Finally, I should like to emphasize that the real object of this research is to produce satisfactory anti-fouling paint. The years are slipping by, and we have not got very far along the road. Excellent work has been done on the protective paint side, but on the anti-fouling side there is a tendency for results to lag. I feel the time has come when a good deal more emphasis needs to be placed on the chemical aspects of this problem, and that it is along this road that success will be achieved. We have paints which are satisfactory when made on the laboratory scale, but what we need to find out now is how to manufacture such paints on the commercial scale, and still obtain the desirable leaching qualities; and that is fundamentally a chemical problem.

Mr. L. F. LEBROCQ (Farnborough): I have only one rather minor point to make on the very valuable paper by Mr. Fancutt and Dr. Hudson. They mention that zinc chromate to B.S.389, 1938, gives considerably better results than zinc tetroxychromate, but they do not give any explanation for the improvement observed.

Thus, zinc chromate supplies to B.S.389/38 is normally of the same type as that supplied to D.T.D. specification 377A. This latter specification is considerably more detailed than the B.S. one and requires the composition of the material

to be substantially that of basic zinc potassium chrome, $K_2CrO_4 \cdot 3ZnCrO_4 \cdot Zn(OH)_2$.

As might be expected from the potassium content, this compound has a moderate solubility in water, *i.e.*, approximately 0.1% calculated as CrO_3 .

The zinc tetroxychromate used by the authors on the other hand had a solubility of only about 0.004% when calculated on the same basis, *i.e.*, it produced an aqueous solution containing only about $\frac{1}{25}$ the amount of the corrosion inhibiting material contained in the solution produced by basic zinc potassium chrome.

This difference in solubility, I feel, has a considerable bearing on the difference between the results obtained with the two compounds.

I should also like to ask the authors whether they have any theories to suggest why basic lead sulphate should be such a good pigment. Is it, for example, a question of lead soaps being formed in a more regular manner than when, say, red lead or white lead is used?

The PRESIDENT (Dr. C. H. Desch, F.R.S.): Can Dr. Baker give any definite information regarding the laminar layer which has been referred to?

Dr. G. S. BAKER: If you take the laminar layer on a fairly large ship, say, of 450 ft., you will find that it is approximately 10μ , or about one-third of a thousandth of an inch. When Professor Harris says that the little organisms which hang on to the paint are about 25μ in size, it means that they are just about twice as large as the thickness of this sub-laminar layer in a turbulent flow. I should like to add, in order to be clear, that I am speaking of the sub-laminar layer and not of what is sometimes called the laminar flow where all the flow is laminar, which occurs only at very slow speeds or when a ship is lying in harbour. That is the kind of thing that you get in a large number of these tests. When the ship is moving you have only a portion of that layer left, and it is of that portion which I am speaking.

The PRESIDENT: That clears it up. I was thinking of something very much thicker than a few microns.

JOINT CORRESPONDENCE.

The INTERNATIONAL PAINT AND COMPOSITIONS Co., LTD. (London) wrote: The further communication on anti-corrosive compositions (by Mr. Fancutt and Dr. Hudson) is welcomed, and the authors and their colleagues are to be congratulated on the very considerable amount of

work which they have carried out under difficult war-time conditions.

Once again we are forced to comment on the fact that sufficient attention has not yet been given to the control of film thickness. The authors are obviously aware of the importance of

this factor (*see* their Fig. 4 and section C), but despite this they still fail to take steps to rule out this experimental error. Since there is no great difficulty in applying a definite weight per unit area under experimental conditions on small plates, it is difficult to understand the reasons for their decision. Until greater control of the weight per unit area is exercised the work will lose much of its value. Reference to Table III. shows in some instances that a 100% difference in weight of paint per panel has occurred and the possible effect of this upon the merit figure can be seen in Fig. 4.

It is unfortunate that the authors should have shown Fig. 7 comparing a proprietary paint with No. 173. The comparison is quite unfair, since the proprietary paint has been applied at only half the thickness of No. 173; had the film thicknesses been equal a very different result might have been obtained.

Again, in the case of the proprietary paint shown in Fig. 8, it seems not unlikely that this particular composition was designed for use over old paint, in which case its performance is good. It should be realized that painting over bare metal and painting over old paint are two different problems and that many manufacturers supply entirely different compositions for the two purposes. A composition used for the wrong purpose might be expected to show failure.

In connection with the tests of proprietary schemes it is of interest to consider the details given in section D(b). Presumably, since the tests were conducted on lines similar to the main investigations, the proprietary schemes would again be at considerably lower film thickness than the Marine Corrosion Sub-Committee controls; despite this, 7 of the proprietary schemes in the case of the freshly weathered steel, and 15 in the case of the old painted steel, have proved superior to A/C No. 174, which paint has the highest merit figure in Fig. 6 and tops the list in the main investigations (Table VI.).

It might be as well at this point to give our experience with A/C No. 173 on small test plates suspended from a raft in the Yealm Estuary. Two coats of anti-corrosive and one coat of anti-fouling were applied on old plates which had been cleaned to metal by scraping and wire-brushing. After 2 months' immersion A/C 173 was showing very serious blistering and failing badly after this short period, while a proprietary scheme was in excellent condition and remained so for a long period. The blisters were not of the fine variety mentioned in section C(2), but were much larger "blebs," up to $\frac{1}{4}$ and $\frac{1}{2}$ in. in dia. This failure was not only found with No. 173 made by ourselves, but also with a paint made to this formulation by another firm in the industry.

It is interesting therefore to consider possible reasons for the vastly different performance of No.

173 at Caernarvon and Millport on the one hand, and in the Yealm Estuary on the other, and its bearing upon ships' painting and immersion conditions. The water in the Yealm Estuary is of varying salinity, and shortly after these plates were immersed there were periods of very low salinity. At Caernarvon and Millport we understand that salinity is high and shows little or no variation. If this varying salinity is the cause of the failure of No. 173, it is of extreme importance and should receive early investigation, since the majority of ships after launching lie in rivers during the fitting-out period and would be subjected to conditions of varying salinity even greater than those experienced in the Yealm. Our experience with paints formulated with media of types A and B is that they are very prone to failure by blistering.

In connection with blistering, we feel that the method of assessment whereby the blistering return is multiplied by *one*, the flaking by *two*, and the rust by *ten*, tends to minimize the blistering defect. Obviously any blistering of the type which we have found with No. 173 is very serious and will leave large areas where the paint is not in contact with the metal; these areas are likely zones where corrosion will start at some later date, possibly after later painting schemes have been applied over loosely or non-adhering old paint.

The Report on Anti-Fouling Research, 1942-44, written by Professor Harris, is exceedingly interesting and quite readable; and it indicates that a fundamental knowledge is being gained by these independent workers into the functioning of anti-fouling compositions. The report should certainly be carefully digested by all engaged in the prevention of fouling on sea-immersed surfaces, with considerable advantage to themselves, and the anti-fouling compositions industry welcomes publications of this nature, where the mode of functioning and the various factors affecting the efficiency of its products are so lucidly described.

The fact that an anti-fouling coating must release gradually a toxin or toxins to the surrounding aqueous medium in order to prevent settlement of fouling organisms has long been recognized by the industry, and it is gratifying to see this so clearly confirmed by other investigators. Proprietary compositions are of course designed with this express object in view, other important factors being the toxic value, solubility, stability, and especially the price of the toxins employed.

The technique of exposure testing seems to be well conceived, and the general application rate of 0.5-0.6 oz./sq. ft., while somewhat heavier than is thought by some workers for small-plate trials to compare exactly with coatings in practice, is a leaning in the correct direction, namely, that a sufficient store of toxin per unit area must be applied.

Section II., dealing with the biological approach to the subject, is of very great interest, and we congratulate the author on this expansion of knowledge of this important and practically significant aspect. The concluding sentence of this section (p. 315 P) could perhaps have been omitted with advantage to the whole, being gratuitous statements on slender data, the probable answer to both (a) and (b) being neither chemical, physical, nor biological, but financial.

The chemical studies on anti-fouling described in section III., involving the mode of action and leaching experiments on poisonous paints, are generally sound, but the "toxicity" tables given in sub-section (3) are open to considerable criticism. While emphasizing the immense amount of work done on the subject, there being no less than 96 compounds listed in Table II. alone, it is exceedingly unfortunate that this data, which doubtless will often be referred to by future investigators, is so misleading and incomprehensible. A study of the toxicity technique employed, translated to the values given in Table I., invites one to believe that mercury thiocyanate will kill 50% of the test organisms in 6 hr. at a concentration of 1 in 1,000,000,000 parts of sea-water, while mercuric chloride requires a concentration 6,000 times as strong to give the same killing power (1/166,000). Surely the explanation cannot be that in one case half the test organisms would have died a natural death in 6 hr. without the assistance of a toxin?

Again, sodium arsenite is given a value of 6.0, presumably indicating that a solution in sea-water of 1/1,000,000 possesses the same killing power as 1/166,000 of mercuric chloride, and is therefore 6 times as effective as the latter—this is quite incredible. It is well known, and moreover expressly stated in the Report itself (see footnote, p. 315 P), that "inorganic" arsenic is almost ineffective as a poison to marine growths, whereas mercury is well recognized as an effective toxin and indeed is generally regarded as possessing from 2 to 4 times the toxicity of copper to most fouling organisms.

Copper sulphate appears with the value 4.6, while copper arsenate, cyanide, salicylate, and thiocyanate are characterized by the value 8.4, which means that the sulphate has to be present at a concentration of 1/40,000 to equal the effectiveness of the other four salts at 1/250,000,000. Here again the unbelievable ratio of 6,000 or more to one appears to operate.

These few examples from the tables cast great doubt on the value of the remainder, and it seems pointless to continue the criticism; some fundamental error in technique or procedure must have affected the results. However, let us consider two organic toxins from Table II., namely phenyl mercuric acetate and nitrate (Nos. 91–92).

Breaking down the toxicity values given, we arrive at the statement that 1/5,000,000 of the acetate has the same effectiveness as 1/100,000,000 of the nitrate, the latter being 20 times as effective as the former. Now, the much less soluble chloride is readily formed on adding either of the above to a chloride solution, and this would logically occur during the toxicity determination in sea-water. The obvious toxin is the phenyl mercuric ion or complex, the acid radical playing little or no part, and it is therefore difficult to believe that the nitrate is 20 times as toxic as the acetate.

Without more information regarding the actual experimental procedure it is difficult to suggest where these enormous discrepancies have their origin, but such factors as *sure* knowledge of the concentrations employed during the test, and relative stability of the toxin over the 6-hr. (or more) period, are obviously fundamentally important. We are convinced that the author himself will agree that a "solution" of copper sulphate of 1/40,000 in sea-water is quite unstable and impracticable, a stable strength being more of the order 1/2,000,000.

In our direct toxicity determinations, a standard of 1/1,000,000 of mercury (as chloride) is used in every case, the relative killing power for 100% mortality of the "unknown" toxin at various dilutions being compared with this standard. From that dilution, which gives a killing time ($\pm 20\%$ is allowed) nearest to the time for the standard, is derived the toxicity of the toxin in relation to mercury. Whenever available, barnacle larvae are used as test organisms, failing which copepods ("acartia") are employed. Throughout hundreds of tests, the standard 1/1,000,000 of mercury gives a 100% mortality in 50–110 min.; this is difficult to reconcile with 50% death in 6 hr. for 1/166,000 mercuric chloride given in Table I. Where toxins much weaker than mercury are involved, the standard may be one-tenth the strength in order to give comparable killing times.

Using this technique, many of the compounds listed have been investigated by us, and it is of interest to note that all the various phenyl mercuric salts have given the same relative toxicity within experimental error, including the chloride. The passive effect of the acid radical in general has been confirmed for several different series of toxins of various types.

The investigators are to be congratulated on their endeavours to assess toxicity values with respect to plant life, which is infinitely more difficult to determine than toxicity to animal life, and the methods of tackling the problem are quite original and encouraging.

Cementiferous anti-fouling compositions (section IV.) present an entirely new departure, and future progress in this direction, after practical

tests on sea-going vessels, will be followed with interest.

The Leaching-Rate Test.

Two methods for the determination of leaching rates of copper and mercury have been published by the Marine Corrosion Sub-Committee:

(1) "Interim Descriptive Statement of the Leaching-Rate Test for Ships' Anti-Fouling Compositions."

(2) "Report on Anti-Fouling Research, 1942-44."

These two methods are the same in principle but diverge, at times considerably, in matters of detail. Both, however, call for some comment on the grounds that the experimental conditions appear at times to neglect factors of quite considerable importance to the assessment of the true leaching rate. These matters are discussed under the various headings below.

The Relation : Area of Paint \times Duration of Test \div Volume of Sea-Water.

It is agreed that this relation is a critical consideration, but what appears to be of fundamental importance is the concentration of copper finally attained in the leaching solution, and for this reason it would appear to be necessary to choose the conditions with some reference to the (probable) leaching rate of the paint under test.

For the test conditions quoted in the first paper it appears that a paint leaching at 10 $\mu\text{g.}$ of copper/sq.cm./day would give a final copper concentration in the sea-water of 0.42 $\mu\text{g./c.c.}$, and at a leaching rate of 15 $\mu\text{g./sq.cm./day}$ the concentration attained would be more than 0.6 $\mu\text{g./c.c.}$

In our experience both these concentrations are too high to permit of the true leaching rate being obtained. Experiments made here some time ago to determine the effect of increasing copper concentration (in the solution) on the leaching rate of a standard anti-fouling composition showed that by the time the concentration had risen to 0.2 $\mu\text{g./c.c.}$ the leaching rate had decreased by approximately 15% from the value obtained by extrapolation of the curve to zero concentration. This was at a pH value of 7.80. At pH 8.0, which is more normal for sea-water, there was evidence that the depression was even more marked, amounting to approximately 25% at a copper concentration of 0.2 $\mu\text{g./c.c.}$ Another feature of these experiments, noted on nearly every occasion, was that where the copper concentration exceeded 0.2 $\mu\text{g./c.c.}$ (up to 1.0 $\mu\text{g./c.c.}$) the apparent leaching rate fluctuated considerably, often rising sharply almost to the original value, only to fall even more quickly to a

point where the rate of solution was negligibly small.

It will be realized of course that these experiments involved the measurement of copper concentrations as low as 0.025 $\mu\text{g./c.c.}$, where the percentage error is liable to be correspondingly high, and consequently no great degree of accuracy is claimed for the results. Nevertheless, the general trend of the results was unmistakable and we have therefore adopted, and venture to recommend, the practice of so arranging the details of the test that the final copper concentration does not exceed 0.2 $\mu\text{g./c.c.}$, and for preference lies between 0.1 and 0.15 $\mu\text{g./c.c.}$

Temperature.

Except under special circumstances, the temperature suggested, 25° C., is too far removed from practical conditions for normal work. Ferry and Carritt* have shown the very considerable effect of temperature changes on the leaching rate of cuprous oxide, and have drawn attention to further effects brought about by the change in pH value consequent upon a change in temperature.

Other disadvantages of working at this high temperature are the probability of a sharply increased rate of dissolution of the varnish medium, and the fact that a varnish film requires some time (often days) to settle down to equilibrium when any alteration is made in the conditions of its environment.

pH Value.

In view of the great magnitude of the effect of hydrogen-ion concentration on the leaching rate of cuprous oxide, as shown by Ferry and Carritt, and which confirms our own experience, it appears to us that insufficient attention to the control of this factor is given in the suggested method.

It is stated that the pH of the sea-water used should be about 8.0-8.2. Between these limits the rate of solution of Cu_2O would, according to Ferry and Carritt, increase by nearly 60% from the lower to the higher hydrogen-ion concentration. It is to be expected, of course, that the properties of the varnish film will modify this effect in greater or lesser degree, but in our experience with normal anti-fouling paints an increase of 30-40% is quite common for the pH range mentioned.

In the suggested leaching method the pH value obviously depends on the carbon dioxide content of the atmosphere, which tends to be high in the ordinary laboratory. It seems worthwhile therefore to draw attention to the necessity, first, to bring all sea-water to equilibrium before use and, secondly, to measure the pH very accurately, making due allowance for any departure from normal.

* *Industrial and Engineering Chemistry (Industrial Edition)*, 1946, vol. 38, No. 6, p. 612.

Storage Conditions.

Storage conditions are of great importance, and immersion in the sea, provided that the salinity is reasonably constant, is much to be preferred. There are two reasons for this preference :

(1) A paint film which has been stored in sea-water where the concentration of copper is appreciable, and is then removed to copper-free water for a leaching test, will nearly always exhibit a false leaching rate, and this effect persists for quite a considerable time, certainly beyond the 4 hours' duration of the leaching test.

(2) Where the solution of cuprous oxide is continuously depressed, as by immersion in solutions already containing copper, the whole character of the immersion-time/leaching-rate curve is likely to be fundamentally altered.

If storage tanks, with their attendant advantages, are to be used, one would suggest that the provision of sea-water nothing short of 200 c.c./sq. cm./day is a necessity, and even more is preferable if the water is available. Any method of overcoming this difficulty would be greatly welcomed, since it would be invaluable to those who have no ready access to unlimited quantities of pure sea-water.

Storage conditions should also provide a degree of agitation sufficient to ensure that processes of diffusion do not limit the rate of solution.

Slime.

The removal of slime accumulations is a difficult problem, and no undue criticism is implied in the suggestion that formaldehyde treatment may be not without adverse effects on many varnish media employed for anti-fouling compositions.

Determination of Copper.

The propensity of copper when in sea-water solution to become adsorbed or otherwise deposited on glass and other surfaces, needs to be borne in mind when conducting leaching trials. It is advisable to avoid contact of the leaching solution with such things as the large pieces of shellac-impregnated cork, as used for holding the plates in position, and also to acidify the solution in the leaching vessel after the test panels have been removed, but before any portion of the solution is removed for analysis. This procedure ensures that any copper adsorbed on the walls of the vessel will be taken back into solution.

In the same way dilute copper standards which have been prepared from copper sulphate and distilled water will lose copper to the walls and bottom of the container. Here again this can be avoided by slight acidification.

Monsieur M. CHARDOME MARDONIE (Marc Chardome, Wilrijk, Antwerp, Belgium) wrote : Mr. Fancutt and Dr. Hudson have conducted their experiments in the line of the truest British scientific tradition. Both the presentation and the discussion of the facts are of a high standard, and the interesting results show the way to a definite improvement in the formulation of protective paints for the ships with which "Britannia rules the waves."

It has been stated that red lead is the best known primer for ships' bottoms, although in the past much has been said for and against its use. I have been told that if a new ships' bottom plate has not been properly coated with red lead, it can be picked out from the rest when the ship is next in dry dock. It has also been said that red lead is a very bad primer for use on ships' bottoms. It has, however, been put forward that the use of red lead should be avoided, at least when the drying time available is short. The coating of ships' bottoms with a bituminous coating (without a priming coat) applied hot by means of a brush, has been suggested and put into practice, apparently with satisfactory results. Further, excellent results from hot sprayed plastic coatings have been reported.

To my knowledge the authors of the paper are the first to tell us positively that a particular paint applied with conventional painting methods and with normal thicknesses, is decidedly better than red lead, zinc chromate, or any kind of normally good proprietary anti-corrosive paint. In addition, they have shown that one pigment, when in admixture with two or three other pigments and in a very wide range of different media—to each of which it shows an extraordinary adaptability, or rather, indifference—allows the formulation of a whole series of priming paints with outstanding protective value.

I am in agreement with the authors' discussion of the effects of variations in paint thickness and notably with their statement "that the comparisons should be based on the paints as they are and not on what they might be." Their statements "good results are not invariably obtained when paint is applied to a freshly descaled surface," and "the returns for blistering were considerably greater for the pickled and weathered specimens because the whole surface was rusted" should also be noted.

The authors are obviously cautious, and quite rightly so, when stating "the formulations in this paper need slight modification for practical purposes, perhaps for use in dry dock, where rapidity of drying is a paramount consideration, but they should be capable of application as they stand for the initial painting of new ships on the stocks, which is the most important part of the ship's history, so far as protection of the bottom plates is concerned."

In conclusion, shipbuilders, ship-repairers, and shipowners should look for relatively quick-drying lead sulphate paints dispersed in media such as *A* or *B*. On the other hand, paint manufacturers should try to develop as soon as possible chlorinated-rubber paints of improved packaging stability, pigmented with basic lead sulphate and an aluminium powder. If this were done, I would not say that we should have less trouble with bottom-plate corrosion than we have to-day, but I am quite sure that it would be reasonable to allow a little longer dry-docking times and to pay higher paint prices.

Dr. D. J. CRISP and Mr. L. JONES (I.C.I., Ltd. (Blacklock and Macarthur), Slough, Bucks.) wrote: We find the work of the Millport team on the assessment of fouling in exposure tests to be of considerable interest and value, and feel that they are working on lines that are fundamentally sound. Much remains to be done, however, before the method can be regarded as being firmly established.

The raft testing of anti-fouling paints is carried out with different objects in view and it is unlikely that the same testing technique will be equally applicable in all cases. The principal uses of the test are:

- (1) The evaluation of new formulations in which one or more factors of a basic formulation are varied.
- (2) The comparison of paints of widely differing formulations.
- (3) The routine checking of batches of the same formulation.

A greater degree of replication will be required for the first and second types of test, where the interaction between the various factors is largely unknown, than for the third type, in which the manufacturer has a background of experience on the particular formulation.

The practice of the Millport team of carrying out tests on small duplicated (or triplicated) patches may be adequate for type (3) tests, but we would question whether this degree of replication is sufficient for types (1) and (2).

In view of the many variables which influence performance in fouling tests, the final results should be presented in such a manner that the whole history of the fouling on both controls and tests can be seen at a glance. For this purpose figured tables are very difficult to compare, and a visual representation of the sequence of fouling of each organism is preferable. While it is realized that such a system of recording results occupies more space than could be afforded in the present Report, it should be emphasized that these data are

essential for any proper understanding of the performance of a particular composition.

It would be of considerable value if we could be given some idea of the significance to be attached to the figures given in the paper for the anti-fouling lives of series of paints.

The lives of a number of paints are given to the nearest day (*see* p. 323 P), each figure being presumably the mean for two or three patches. Without some idea of the standard error of the mean, the figures must remain of limited value to the reader. Again, what sort of agreement could be expected if the tests were carried out at the same site but at different times or simultaneously at different test sites on (a) the same paint or (b) on different batches of the same formulation?

The practice of including one or more non-toxic patches is commonly adopted and is a good one so far as it goes, but have the authors considered the use of a standard formulation of which a batch is made at the same time as the experimental paints? We have no doubt that attention is being paid to many of the points we have raised, but without some such measure of the reliability of the test, the results quoted in the paper must remain largely subjective.

The above remarks were partly prompted by a statement published elsewhere* that "the reason for the failure of the Marine Corrosion Subcommittee's anti-fouling paint was that the copper leaching rate of the paint as manufactured on a commercial scale was found to differ considerably from that of the laboratory sample and to be only half of the critical rate necessary to prevent fouling."

The reliability of raft tests has many parallels with that of exterior exposure tests on paints, an ever present problem with paint technologists, as will be seen by a study of the paper by Jolly† and others.

Settlement of Fouling Organisms.

Professor Harris has collected a most useful and concise summary of the salient features of the common fouling organisms.

The comparison of times of settlement of organisms in different localities is of practical importance, and it is to be hoped that fuller details of these observations, giving actual dates and specific names, will become available. Observations we have made in a number of localities indicate that the breeding season in the south-east is an extended one; while it begins somewhat later than in the south-west, it continues well into October.

It would be interesting to know to what extent the reported absence of particular organisms (*e.g.*,

* J. E. Harris and W. A. D. Forbes, *Transactions of the Institution of Naval Architects*, 1946, vol. 88, p. 240.

† V. G. Jolly and others, *Journal of the Oil and Colour Chemists' Association*, 1940, vol. 23, p. 356.

barnacles at Plymouth) is due to the larvae being washed away from the raft site or to local unfavourable conditions for breeding in a particular season. If the latter explanation is ruled out, as seems likely, it is clear that raft sites should be very carefully chosen in relation to tidal currents and areas likely to produce infection.

The Sub-Committee's experience of animal fouling organisms agrees closely with ours, except in one or two details. For instance, we have not observed the settlement of *B. balanoides* on test or control panels and indeed have found continuous immersion to be fatal to young spat. It has also been observed that while thick scum, silt, or slime reduces settlement of barnacle cyprids, settlement is favoured by the existence of a very small amount of deposited or possibly of adsorbed material.

"Border Effect" and Laminar Flow.

Although we have only performed a limited number of experiments of the type described in section II. of the Report, the border effect described has not been observed. Perhaps the velocity of water currents in relation to the leaching rate is very critical to obtain such an effect. However, on other grounds it does not seem possible without further evidence, to accept the "laminar layer" theory as a general mode of action of anti-fouling compositions. In the first place, the layer of laminar flow next to the paint surface is not a stationary layer; it is in fact in this layer that the velocity gradient is highest. Although from the point of view of hydrodynamic treatment it may be possible to consider this layer as stationary, this is not permissible when its chemical constitution is under discussion, and the high velocity gradient would be expected to reduce the concentration gradient in this layer very rapidly. In other words the "concentration boundary layer" will be very much thinner than the hydrodynamic boundary layer, perhaps amounting in practice to what would be indistinguishable from contact poisoning. Secondly the laminar-layer theory appears to involve very much greater sensitivity to the effects of surrounding water velocity, distance from edge of plate, and proximity to obstacles, than is in fact observed. Thirdly the anti-fouling action should, according to the laminar-flow hypothesis, be dependent only on the copper leaching figure, and independent of the nature of the surface. Nevertheless it has been shown* that the critical leaching rate of certain copper alloys is much higher than that given in this paper.

It is possible that the mode of action of anti-fouling compositions is not the same for all organisms and the laminar layer may be of limited application. Careful work is clearly needed to give information of the mode of transport of

poison from the paint film to the organisms in every case.

It should also be emphasized that the correlation between leaching rate and anti-fouling activity is not yet sufficiently and generally established to lend argument to the laminar-layer theory. A rough correlation is likely, whatever may be the mode of action of the poison, and such a correlation is in itself no proof of a causal relation between leaching and toxic action, since both phenomena may be parallel results of changes in toxin concentration or mobility in the paint.

Organic Poisons.

Toxicity data given in Table I. raise many interesting problems to which no doubt attention has been given; for example, why is the range of toxicity of copper and mercury compounds so dependent (apparently) on the accompanying anion, and why the remarkable difference in toxicity between tetramethyl and tetraethyl thiuram monosulphide?

The results given for the anti-fouling performance of the large and miscellaneous collection of poisons are very interesting as a preliminary survey, but it is regretted that the milling technique was admittedly poor and that only one vehicle was employed. The influence of vehicle and particle size is so important that none of the poisons represented should be ruled out entirely by its performance in so limited a test, and the lack of correlation between toxicity and anti-fouling tests may be due to these factors.

Leaching Tests.

We do not find the evidence presented in the paper on the correlation of the results of the "leaching test" with the anti-fouling performance of the paint to be very convincing. Earlier in the paper (p. 304 P) it is emphasized, and rightly so in our opinion, that "the criterion of failure of a test area by fouling should be a clearly defined 'all-or-none' matter." Turning to Fig. 3, however, we find that the fouling is rated in arbitrary units. Of the 14 paints tested, 13 fouled and on the other one fouling was negligible. The latter was the only paint to have a "leaching rate" above 10. It would have been more convincing if we had been given the leaching rates and anti-fouling performance of a series of paints in which those having rates above and below 10 were approximately equally represented. It is claimed that Fig. 5 shows the correlation between leaching rate and fouling on a number of commercial compositions. All except two contained mercury and it is not clear whether the copper or mercury leaching rates, or both, are referred to. It is admitted earlier that the leaching rate of mercury from copper-mercury paints is very variable and un-

* F. L. Laque and W. F. Clapp, *Transactions of the Electrochemical Society*, 1945, vol. 87, p. 103.

connected with the anti-fouling efficiency. By this, of course, the author infers, not that mercury has no anti-fouling effect, but that this effect *does not correlate* with its leaching rate. It is difficult to see therefore how the author can claim that the figure shows any correlation.

We are unable to agree with the author's conception of a copper leaching figure which is characteristic of a given paint. The curve shown in Fig. 9 may well be characteristic of a series of formulated paints which are admitted to have been poorly dispersed, but it is by no means characteristic of rosin-based anti-fouling paints in general. The important point is that on the basis of this curve an average of the leaching figure obtained after 30 and 60 days has been adopted by the author for predicting the anti-fouling performance of paints (p. 324 P).

Reference to Fig. 5 shows how little this average figure could be said to be characteristic of the majority of the commercial paints tested. The same would be true of the four typical paints for which leaching curves are given in a paper by Ketchum * and others, and for the curves given in a later paper † from the same laboratory on the "Action of Anti-Fouling Paints."

The following conclusion of these authors which is given in their first paper cannot, in our opinion, be too strongly emphasized: "It is obvious from this data that the leaching-rate determination is characteristic of the paint *only at the time the measurement is made*. It is not possible to predict the future behaviour of a paint from any single leaching-rate determination." * It is significant that where the American workers calculate an average leaching figure they ignore the results obtained below 2 months. The reason for this will be obvious from an inspection of their curves.

The results given on pp. 322 P–324 P are, however, based on the average of the results for 10, 20, and 30 days after immersion, and we would question whether they can be claimed to set out any general principles. They are merely indications which are liable to be reversed when an extended leaching curve is obtained. It is, of course, true that if a paint is unsatisfactory as regards leaching in the early stages of its life, then its later history is of little importance.

The above comments and criticisms are offered in the hope that they will be found to be of interest.

Mr. L. JONES (I.C.I., Ltd. (Blacklock and Macarthur), Slough, Bucks.) wrote: I have studied with considerable interest the mass of valuable

information collected in the paper by Mr. Fancutt and Dr. Hudson, and would like to offer the following comments:

Index Figures.

We have found the authors' conception of an index figure useful in our work on the assessment of anti-corrosive compositions, but abandoned the practice of recording the percentage of each type of failure (blistering, flaking, rusting, &c.) to the nearest unit, early in our work. In our own experience there is a high personal error in making assessments on a raft to within a unit per cent, even with the aid of a grid (Perspex) which has 1-in. squares marked on it. This holds both for assessments made by the same inspector after an interval of a few hours as well as for those made by different inspectors at the same time.

Weighting.

There is always room for differences of opinion as to the relative weightings to be attached to the various defects and it would be interesting to have the authors' reasons for increasing the factor for rusting from 4 to 10. If the intention was primarily to reduce the influence on the index figure of the blistering which was apparently widespread over previously rusted areas, I feel that this is not a desirable step and would retard the development of compositions free from this defect.

It is said in the paper that fine blisters invariably form on a paint film over the areas where it lies on a previously rusted surface. We have found a number of exceptions to this statement both in our raft tests and in tests at Slough using a rotor apparatus ‡ developed at the Chemical Research Laboratory, D.S.I.R., Teddington.

The method of comparisons used (p. 280 P) suffers from the fundamental disadvantage that correlation with other and previous tests is rendered difficult, if not impossible.

Spreading Rates.

It is true that a proprietary system is included, which in previous tests proved to be well above the average for commercial compositions, but this was applied presumably at the "natural spreading rate" on small panels.

In formulating their compositions the authors deliberately made the spreading rates lower (by solvent adjustment) than in previous tests so as to reduce the disparity in this respect between the small specimens and actual ships. The proprietary compositions on the other hand were

* B. H. Ketchum, J. D. Ferry, and A. C. Redfield, *Industrial and Engineering Chemistry (Industrial Edition)*, 1945, vol. 37, p. 456.

† B. H. Ketchum, J. D. Ferry, and H. E. Burns, *Industrial and Engineering Chemistry (Industrial Edition)*, 1946, vol. 38, p. 931.

‡ Bengough, Wormwell, Yardley, and Nurse, British Patent No. 569,342.

presumably intended for application to ships and not small tests panels. The comparison would have been better had steps been taken to make allowance for this. As it is, the total dry film weights were only half those of the experimental compositions.

It would also have been desirable to include a few of the best compositions reported in Part I.* applied at the same film thicknesses as were used originally, which were between one-half and two-thirds of those in the latest tests.

The authors comment that "the use of the former standards of assessment would have proved insufficiently sensitive to distinguish clearly between the majority of the paints." The very real danger here is, of course, that the present method lends itself to the drawing of conclusions on the basis of apparent numerical differences in merit figures for which there is no logical justification.

I am unable to agree with the authors' conception of a *natural spreading rate* for the following reasons:

In the description of the preparation of the paints, it is pointed out that they were allowed to stand for one week, after which the consistency was adjusted where necessary by the addition of naphtha. The criterion for making any adjustment was a brushing-out test. This adjustment is looked upon by the authors as legitimate and few paint formulators would disagree. Once the principle of consistency adjustment by the addition of solvent is admitted, however, it is hardly possible to maintain that the resulting spreading rate is characteristic of the paint formulation.

The fundamental formulation is surely that of the non-volatile portion of the liquid paint, the volatile solvent playing only a transitory part. That the natural spreading rate is a very arbitrary figure is tacitly admitted by the authors when they point out that the spreading rate was deliberately made lower than in the previous tests so as to reduce the disparity in this respect between these small specimens and actual ships.

It is true that there are other means of adjusting the spreading rate than by an addition of solvent, but this does not alter the fundamental argument that the resulting spreading rate is an arbitrary figure which is influenced largely by such factors as the size of brush used, nature of surface to be painted, personal differences, &c. All that can be claimed is that if these conditions are controlled as closely as possible for any given series of paints, then the spreading rates will be very roughly characteristic of each paint as used.

The extent of variation experienced in the natural spreading rate for one particular composition (AF 10/43) will be appreciated from the following figures. This composition was applied

to 123 panels coated with different anti-corrosive compositions. The spreading rate (square yards per gallon) varied from 37.3 to 74.6, a range of 37.3 (Table III.). The corresponding figures for film thickness are 83.5 μ to 41.7 μ , or a range of 41.8 μ (calculated from data on p. 275 p.).

This is largely a measure of the personal factors involved in the painting of the panels. There is no reason to suppose that the variations, due to similar causes, for the anti-corrosive compositions are not equally large, so that the range in total paint film thickness recorded in Fig. 4 (*i.e.*, 53 μ) might well be due to errors in painting and not to intrinsic differences between the compositions.

The figure of 53 μ is, of course, less than the true range, since it is based on the average film thicknesses for pairs of specimens (the film thicknesses for the individual specimens are unfortunately not recorded in the paper), but this correction would not materially affect the argument.

The problem of making allowances for differences in film thicknesses between the test panels is admittedly a difficult one. In raft tests, using large panels, it is impossible to exercise as close a control over film thicknesses as would be desired, and this makes it all the more imperative that there should be adequate replication on each type of surface being studied. Only in this way can the significance of minor differences due to formulation variations be established.

Zinc Oxide Series.

When studying a large series of results such as the authors have presented, two important questions arise: The first is whether the differences in merit figures, upon which many conclusions are based, are real or merely due to chance. The second is to what extent does a particular pigment effect depend on the medium under consideration and *vice versa*. As a corollary to this we have the problem as to what extent do the pigment and medium effects vary according to the particular surface of the test panel, *i.e.*, I. or II.

It will be obvious that if the difference between the means (or totals) of, say, two pigment series is large compared to the scatter within each series, then the pigments differ significantly in their behaviour. On the other hand if the difference between the means (or totals) is small compared to the scatter of the individual results, it provides no evidence that the pigments do in fact differ significantly.

Statistical methods are of use in such doubtful cases to determine the probability as to whether or not the differences recorded are due to real differences in behaviour between the pigments. The technique known as the "analysis of variance," of which the *t* test is a special case, provides

* F. Fancutt and J. C. Hudson, *Journal of The Iron and Steel Institute*, 1944, No. II., p. 269 p.

the appropriate tests of significance. It may be objected that this method of treatment is not applicable to *merit figures* which are derived only indirectly from the original measurements (*i.e.*, blistering, flaking, rusting, &c.). This objection would have some substance if the method were being used to establish the significance of apparent differences. In the present instance, however, the method is being used only to show that many such differences are not significant. If they are shown not to be so by this method, then *a fortiori* they are not significant when we take their origin into consideration. A number of significance levels for pigment and medium effects have been calculated incidentally, but these are subject to the above limitations and should be treated with caution. It would have been preferable to carry out the analysis on the original index figures, but these are not available in the paper.

Application of the method requires the results to be set out in a form similar to that of Table VII., but with the merit figures for each surface (I. and II.) separated. In Table VII. the authors show the totals for each pigment combination (columns) and each vehicle (rows), together with the grand total. In the analysis of variance we convert these totals to means and proceed to analyse the variations between and within the column and row means and within the grand mean. This gives us a measure of the variation in the grand mean due to the pigment, medium, and surface effects, and to the residual errors. By calculating separately the ratios of the pigment, medium, and surface variations (or variances) to the residual error variance (Fisher's *Z* test), we are able to assess their relative significance. It will be clear that the greater are the variations due to residual errors, the greater must be the variations due to pigment or medium effects if they are to be significant.

The results for the zinc oxide series recorded in Fig. 6, excluding vehicles *E*, *F*, and *G*, which were tested with one pigment combination only, have been subjected to such an analysis and the results are given in Table A.

TABLE A.—*Analysis of Variance for the Zinc Oxide Series.*

Source of Variation.	Degrees of Freedom.	Sums of Squares.	Mean Squares.
Between media (<i>M</i>) .	3	23.6	7.87
Between pigments (<i>P</i>) .	3	6.8	2.27
Between surfaces (<i>S</i>) .	1	11.8	11.8
<i>M</i> × <i>P</i> interaction .	9	25.3	2.81
<i>M</i> × <i>S</i> " .	3	17.1	5.70
<i>P</i> × <i>S</i> " .	3	4.4	1.47
Residual	9	19.2	2.13
Total	31	108.2	...

* See R. A. Fisher, "Statistical Methods for Research Workers." London, 1946: Oliver & Boyd.
1946—ii

The *M* × *P* interaction is a measure of the extent to which the *M* (medium) effect depends on the particular pigment (*P*), and conversely. The word interaction is here used in a statistical and not the chemical sense; similarly for the other interactions. The residual variance can be regarded as a measure of the errors at the testing stage and includes errors due to varying film thicknesses, errors in assessment, &c. The possible second-order interaction (*M* × *P* × *S*), if it exists, will also be included in this term.

Continuing the analysis with the aid of Fisher's variance-ratio *Z* test we find that:

- (1) The *P* × *S* and *M* × *P* interaction effects are below the 0.20 significance level.
- (2) The *M* × *S* interaction is below the 0.05 significance level, but is suspiciously large.
- (3) The *M*, *P*, and *S* main effects are all below the 0.20 significance level.

It is therefore concluded that for this series *as a whole*, the differences in merit figure due to the main pigment, medium, or surface effects are not significant and no general conclusions can logically be drawn.

This, of course, does not invalidate the statement of the authors that the distinction in merit figure between the paints of the basic lead sulphate series, as a class, and those of the zinc oxide series, as a class, is clear-cut and definite. Since the *M* × *S* interaction is suspiciously large we have broken down Table A into separate analyses for each surface, as shown in Table B.

TABLE B.—*Analysis of Variance for each Surface. (Zinc Oxide Series.)*

Source of Variation.	Degrees of Freedom.	Surface I.		Surface II.	
		Sums of Squares.	Mean Squares.	Sums of Squares.	Mean Squares.
<i>M</i>	3	10.5	3.5	30.7	10.23
<i>P</i>	3	8.5	2.83	3.2	1.07
Residual .	9	16.0	1.78	28.0	3.11
Total . .	15	35.0	...	61.9	...

Applying the *Z* test as before we find that:

- (1) For surface I., the medium and pigment main effects are below the 0.20 significance level.
- (2) For surface II., the medium effect only is significant (0.05 level).

This does not necessarily mean that the difference between the total merit figures for any two media (on surface II.) is significant. The latter point can only be established in doubtful cases by use of the *t* test.

Applying this to the results for media *A* (total merit figure, 3) and *B* (total merit figure, 18), we find only a slight indication that medium *B* is superior to medium *A*. In a similar manner it can be shown that the indications that *B* is superior to *C* and *D* are weaker still. The statement of the authors that, in the zinc oxide series, medium *B* was the most satisfactory of the four media tested therefore requires some modification, as also does the statement that zinc tetrahydroxy-chromate proved markedly inferior to zinc chromate.

Basic Lead Sulphate Series.

The results for the basic lead sulphate series (media *A* to *D*) and the first five pigmentations in Fig. 6) have been examined on similar lines.

The results of the analysis of variance are shown in Table C.

TABLE C.—*Analysis of Variance for the Basic Lead Sulphate Series.*

Source of Variation.	Degrees of Freedom.	Sums of Squares.	Mean Squares.
Media (<i>M</i>) . . .	3	348.68	116.23
Pigments (<i>P</i>) . . .	4	20.90	5.23
Surfaces (<i>S</i>) . . .	1	15.63	15.63
<i>M</i> × <i>P</i> interaction . . .	12	149.70	12.48
<i>M</i> × <i>S</i> . . .	3	27.07	9.02
<i>P</i> × <i>S</i> . . .	4	44.50	11.13
Residual . . .	12	41.30	3.44
Total . . .	39	647.78	...

Applying the variance ratio test as before we find that all the interaction effects are suspiciously large and cannot be ignored.

There is no rigorous test to demonstrate the existence of pigment and surface main effects. The medium main effect can be shown to be significant, a fact which is obvious from inspection of the results. It is therefore necessary to break-down the results into separate analyses (*a*) for surfaces and (*b*) for media; these analyses are shown in Tables D and E, respectively.

Applying the variance ratio test to Table D we find that only the medium variations are significant. The pigment variations are below the 0.20 level of significance for both surfaces.

TABLE D.—*Analysis of Variance for Each Surface. (Basic Lead Sulphate Series.)*

Source of Variation.	Degrees of Freedom.	Surface I.		Surface II.	
		Sums of Squares.	Mean Squares.	Sums of Squares.	Mean Squares.
Media (<i>M</i>) . . .	3	257.2	85.73	118.55	39.52
Pigments (<i>P</i>) . . .	4	31.7	7.93	33.70	8.43
Residual . . .	12	128.3	10.70	62.70	5.23
Total . . .	19	417.2	...	214.95	...

Similarly we come to the following conclusions from Table E:

Medium A.—The pigment variations only are significant (0.01 level).

Medium B.—Neither the pigment nor surface variations are significant. This is clearly due to very high residual (including interaction) errors.

Medium C.—The surface effect only is significant (0.05 level).

Medium D.—Neither the pigment nor surface effects are significant.

The above analyses serve to emphasize the statement of the authors that certain of the conclusions in the paper regarding pigmentation (and media) should be treated with caution.

Only in one medium (*A*) out of the four considered (*i.e.*, *A* to *D*) are differences due to pigment variations significant. Even here there is no evidence that zinc tetrahydroxy-chromate is inferior to zinc chromate. It can also be readily shown by the *t* test that the claim that on the whole the basic-lead-sulphate/aluminium/extender combination has proved best, cannot be substantiated. The statement "In the basic lead sulphate series, barium chromate gave the best results of the three chromate pigments" can apply to medium *A* only, and even here the evidence is doubtful.

Graphite and Mineral Black Series.

It is difficult to make any serious comments on the results for this series, since the individual merit figures for each panel are not given in the

TABLE E.—*Analysis of Variance for Each Medium. (Basic Lead Sulphate Series.)*

Source of Variation.	Degrees of Freedom.	Medium A.		Medium B.		Medium C.		Medium D.	
		Sums of Squares.	Mean Squares.	Sums of Squares.	Mean Squares.	Sums of Squares.	Mean Squares.	Sums of Squares.	Mean Squares.
Surface . . .	1	0.1	0.1	0.1	0.1	36.1	36.1	6.4	6.4
Pigment . . .	4	59.4	14.85	69.4	17.35	27.4	6.85	14.4	3.6
Residual . . .	4	3.4	0.85	71.4	17.85	19.4	4.85	23.6	5.9
Total . . .	9	62.9	...	140.9	...	82.9	...	44.4	...

paper. Failing these we have no estimate of the errors and without the latter we cannot estimate the significance of the apparent differences such as are recorded in Table VIII.

However, in view of the admission that the effect of the surface condition of the specimens was more pronounced in the paints of this series than in those of the other series, I would hazard the opinion that the results given in the Table and the conclusions drawn from them should be treated with considerable caution.

It is unfortunate that the war conditions under which the researches were carried out prevented the authors from giving greater consideration to the effect of film thickness. As they clearly recognize, they have now reached the stage of attempting to improve upon what is basically a satisfactory formulation (Paint No. 32 of the earlier series) and the film-thickness effect is becoming increasingly important.

That this stage has been reached by other workers in this field is shown by the following extract * :

“A series of randomized and replicated tests was recently applied to the exterior areas of small patrol craft. The purpose of the tests was to determine under actual operating conditions any important differences in performance between a selected group of primer pigment formulations.

Recent observations of these tests indicate that specific combinations may have less influence on primer performance than does the film thickness.

In this test small differences in formulation seemed to be of little moment in the protection of the metal.

Some observers feel that the tests may indicate that the differences between competitive primer pigments may not actually be as great as had been reported in some of the literature.”

The above comments are offered in the spirit of constructive criticism and in the hope that they may be found to be of some interest and value.

Mr. R. H. TRUELOVE (The Red Hand Compositions Co.) wrote: The authors of these three papers are to be congratulated on a fine presentation. The records show great care and attention to detail, and the findings therefore become very valuable, particularly to the uninitiated. In general, the conclusions are well supported by the facts and experiments quoted.

The several techniques are given with such precision that there should be no difficulty in other investigators reproducing the results or amplifying the work.

In fairness to the old-established industry of ships' bottom composition manufacture, we must say that there is but little in these papers which would lead those now supplying the demands of shipowners to modify their procedures, which, in our case, at least, are the result of the work of our own research team for decades.

The industry is well aware of the possibilities of improvement in performance, which has been possible technically for a lifetime, but which is prevented by the truly shocking conditions under which painting usually has to be performed in the docks, and the price which consumers have hitherto been prepared to pay.

Some of the matters dealt with call for comment and discussion, and so we append some remarks relating mainly to the Report on Anti-Fouling Research, 1942-44, by Professor Harris.

Unfounded condemnation of proprietary compositions, to which manufacturers are, unfortunately, becoming accustomed in these papers, still persists, though possibly in a lesser degree than in earlier writings.

The decision to rate anti-fouling compositions on plates on the type of fouling, however light, rather than on the quantity, is sound scientifically. The ultimate quantity of growth on a ship, however, must remain the criterion of success in practice. The former system does indeed serve to assess the power of the coating to resist fouling organisms under uniform static conditions, but the latter is affected by many other factors.

Most of the assessments of fouling in these papers have been based on minute organisms, whereas such growths are not considered as “fouling” on a ship. It is the larger organisms, such as *enteromorpha* and barnacles, that follow long after the smaller ones, which count as “fouling” on ships; they may take many times longer to appear. Thus a shipowner would describe as “nearly clean” a vessel with slime only, whereas the scientists have been classing this as foul. This difference of view is exemplified by the report of the Clyde steamers (see p. 304 P, section (4)). A few barnacles or hydroids on a ship do not constitute a “foul bottom” in dock parlance. Consequently the effective life of commercial anti-foulings is in practice far greater than the authors indicate.

The data on leaching-rate tests are fully given as far as stationary conditions are concerned, but it is obvious that these are far from having any practical application as yet.

We agree, and indeed discovered many years ago, that surfaces in static tanks lose poison less rapidly than on moving ships in the sea. We also have been exploring methods of overcoming this difficulty, and consider that ground-glass plates, coated with composition, bolted to

* H. Nelson, “A Summary of Wartime Experience with the Problem of Painting Ships of the Fleet.” National Paint, Varnish and Lacquer Association, Inc., Scientific Section, 1945, Sept., Circular 710.

the bilge keel of sea-going vessels, give results which must be most closely related to those obtained on the bottom of the ship itself.

It is as a result of practical tests on ships' bottoms, after laboratory evolution and plate tests, that we base our proprietary brands, and for this reason we claim to obtain good results in practice.

Leaching-rate tests have been made on films of thickness less than is common on ships, for the latter are indeed very heavy coatings. Thus the life on ships may be far greater than leaching-rate tests, as quoted here, imply.

The information obtained of the settling of microscopic forms is very interesting, and it must be agreed that the interpretation of the sequence of growths and the consequent insight into the degrees of anti-fouling potency are very valuable.

To use the onset of *Tubularia* as a criterion of anti-fouling virtue, as in Fig. 5, is not justifiable. The author of the paper on his own showing agrees with this (*see* p. 304 P), for it is said that this organism is much more resistant to poisons than are those which usually cause ship fouling, such as barnacles, &c. Thus, if *Tubularia* are ignored, nearly all the proprietary compositions tested, and then condemned, have, in fact, been satisfactory.

Perhaps, also, too much stress is laid on the effect of diatomaceous slime, &c., both as a criterion of fouling itself and in its inhibition of other fouling forms. This is naturally the consequence of the tests having been made on stationary plates. On ships' bottoms these diatoms are much less prevalent, and their adhesion to a rapidly moving surface is insufficient for their perpetuation.

The opinion expressed regarding bacterial slime actually preventing barnacle growth, carries with it the corollary that, if this slime could be encouraged sufficiently on a paint, poisons might be superfluous. It implies also that, where bacterial slime can form, the copper emission rate, as obtained by the leaching of clean surfaces, is less significant than it would seem. The leaching rate is greatly depressed by the slime during its presence, leaving thus a greater reserve of poisons for other periods when the slime is not present.

Manufacturers of ships' compositions will note the acknowledgment in the first paragraph of section (3), where it is appreciated that there are a number of successful commercial anti-fouling compositions.

The figures under the heading "Fouling on Ships," section (6), are, in our view, misleading. The bad results quoted of thirty voyages are not representative, in our opinion, and for comparison we give our records of sixty vessels, being ships operating in West African waters, the Indian Ocean, and the Mediterranean. These particular

voyages are exceptionally severe on anti-fouling paints, and the details were collated in wartime, when ships were often lying for long periods in very fertile waters :

Condition.	Percentage.	Average Duration of Voyage, days.
Clean	40	230
Lightly fouled	40	280
Foul	20	280

A random selection of two-hundred vessels, operating in all waters, including the above, gives an overall picture of the results obtained with the ordinary commercial compositions :

Condition.	Percentage.	Average Duration of Voyage, days.
Clean	60	270
Lightly fouled	23	300
Foul	17	330

The classification "clean" allows that insignificant slime may have been present. The classification "lightly fouled" implies the presence of fouling organisms in sufficient numbers to warrant recording, though insufficient to arouse comment by the Marine Superintendent. "Foul" does not necessarily mean that the growth was general or very heavy up to the time of inspection, but that further voyaging without re-coating would have been uneconomic.

The conclusions reached on p. 323 P, regarding the effect of copper content on leaching rate and on the life of the composition, are quite definite for the given conditions, but the figures for leaching rate are obtained after such a long period that they cannot be looked upon as constituting an accelerated test, nor be interpreted as representing the behaviour of a composition in service. It must be appreciated that the leaching rate and the life will be very different for different thicknesses of anti-fouling. Thus at the great thickness often used in commerce, a sufficiently high emission of copper may continue from the lower layers of the paint after the top layer has become exhausted. The surface layer then functions as a check on too high a rate of loss of the metal. This factor may serve to explain why paints which fail on a raft, succeed on a ship.

Regarding organic compounds, we find our past records to agree with the data given, generally. We have found, too, that the high toxic value obtained in laboratory experiments is not substantiated when field tests are made. We supplement with a few of our records of toxicity figures, which were obtained with barnacle nauplius; these were done many years ago when we adopted a 3-min. interval, with 90% deaths (*see* p. 357 P).

In Table F we give records of some further organic compounds, prepared in our laboratories many years ago, which, however, did not bear out in paints the promise of potency shown in the laboratory growth tests, yet the explanation of

Compound.	Toxicity to Barnacle Nauplius.
Diphenylarsenic acid	6.6
Nitrophenyl mercuric chloride	6.4
Chlorpicrin	4.7
Mercuric chloride	4.5
Diphenyl-cyano-arsine	6.7
Methyl phenyl phenarsazine	6.3
10-Acetyl phenarsazine	6.4
Tolyl mercury chloride	6.5
Phenyl mercury chloride	6.5
Chlorphenarsazine	6.7
Cacodylic acid	2.3
Copper sulphate	4.0

such failures given in the text of the paper cannot apply to those particular compounds, as they are relatively insoluble in the paint solvent.

TABLE F.—Effect of Some Organic Compounds on the Growth of *Nitzschia*.

Concentration of Compound, $\mu\text{g./c.c.}$:	0.01.	0.02.	0.05.	0.1.	0.15.
Compound.	Relative Count of <i>Nitzschia</i> .				
Chlorphenarsazine	1
7-Chloro-7 : 12-dihydro- benzo-phenarsazine	20	1
12-Chloro-7 : 12-dihydro- benzo-phenarsazine	26	4	1
7-Chloro-7 : 14-dihydro- disobenzo-phenarsaz- ine	60	56	38	26	1
14-Chloro-14 : 7-dihydro- dibenzo-phenarsazine	66	64	58	48	32
Non-toxic control	← 68 →				

As regards the estimation of leaching rates of organic toxic compounds, we have found that growth curves on *Chlamydomonas* or *Nitzschia* under standardized conditions of light and temperature on leached extracts from compositions, yield reproducible results, which agree fairly well with the final analysis of the residual film. The effect of copper is not additive under these conditions.

Thus, in the use of chlorphenarsazine, the results in anti-fouling compositions are that this compound leaches out at a fairly steady rate :

		Leaching Rate, $\mu\text{g./sq. cm./day.}$	
	Chlorphen- arsazine, mg./sq. cm.	By Analytical Figure.	By Growth Test.
Anti-fouling <i>A</i>	1.59	1.9	1.9
Anti-fouling <i>B</i>	0.9	3.4	2.0
Anti-fouling <i>C</i>	0.8	4.0	4.6

The method is of interest, as it can be applied to organic toxic compounds, which cannot be estimated by chemical analysis.

On p. 319 P the statement is made that the undercoat does not affect the emission rate of copper, but in commercial paints the undercoat does sometimes affect the leaching rate, especially when not fully dried off, as often occurs in

practice. Below we give figures illustrating this :

	Leaching Rate, $\mu\text{g./sq. cm./day.}$
One anti-fouling coat	16.6
Anti-fouling coat over itself	23.7
Anti-fouling coat over rosin primer	18.5
Anti-fouling coat over bituminous primer	13.1
Anti-fouling coat over bituminous primer, after 4 hr.	10.8

Therefore we contend it is necessary to consider the anti-fouling and its undercoat as one system.

The data on the making of leaching-rate tests is all that could be desired, except for one recommendation which does not seem at all a safe procedure.

The immersion of compositions in formalin is likely to change entirely the chemical nature of the compounds present, for formalin is well known to chemists as a very powerful reducing agent, converting some oxides and salts to the metals or, at least, to a lower state of oxidation. Also, formaldehyde combines with organic matter, and is well known as the active ingredient in the formation of some synthetic resins.

Respecting the generally accepted and quoted figure of 10 $\mu\text{g.}$ of copper per square centimetre as being sufficient to prevent fouling, it should be borne in mind that copper may be absorbed by organic matter, whether living or dead, in very contaminated waters. This rate of emission might not then be adequate, because of a lowering of the concentration of copper, leaving insufficient to poison all of the postulated high concentration of organisms. This state of affairs may possibly obtain on the West Coast of Africa, where some anti-fouling compositions, effective in other parts, are known to become foul.

Referring to Figs. 7 and 8 in Mr. Fancutt and Dr. Hudson's paper, it must be appreciated that proprietary paints during wartime had to be made with the materials which were available in sufficient quantities, and they have always had to meet a competitive price. Moreover, practical primings have to dry very rapidly, and to be of thin consistency, to meet docking conditions, whereas the paints with which they were compared required time for the linseed oil to oxidize and were, no doubt, of thicker consistency. It is for these reasons that the proprietary composition has proved less protective on the plates illustrated than has the special formula.

The recognition, in another part of the paper, that the nature of the medium of an anti-corrosive paint is of overriding effect, is timely, for sometimes too much importance has been given to the pigment constituents.

We are particularly glad to note that chlorinated rubber has been given a very high place among possible media for anti-corrosives. This Company has, for a decade, had such a primer "Latenac"

in the market. It has not been much used, as shipowners have been reluctant to pay the price.

The incorporation of Burntisland red in the paints may have introduced alkaline effects. Ordinary Burntisland red contains a considerable quantity of sodium, probably as aluminosilicate, which allows of a leaching of as much as 10 mg. of NaOH per gram of the pigment. In order that the ingredient used in the anti-corrosive

paints may be accepted as an "inert" filler, some reassurance on this point is called for.

In conclusion, once more we must express appreciation of the great amount of meticulous research that has been done by the investigators. Our comments give a somewhat different angle on the problem here and there, but nothing can detract from the self-evident excellence of the work reported in these papers.

AUTHORS' REPLIES.

Mr. FANCUTT and Dr. HUDSON wrote in reply :

(1) We thank Dr. Wormwell for his contribution and in reply to the query regarding deterioration at the edges of the specimens, find that on the whole, the behaviour of the painting schemes at the edges links up satisfactorily with the rating deduced from the surface inspection. For example, the painting schemes based on anti-corrosive compositions formulated with the chlorinated-rubber medium were observed to be practically intact at the edges at the completion of exposure, in conformity with their excellent behaviour on the surface of the specimens proper.

(2) We are glad to have Dr. Wormwell's confirmation that, within limits, film thickness is not necessarily a determining factor so far as the merits of painting schemes of widely different types and formulations are concerned. This is in general agreement with our own views and observations over a period of years.

(3) We agree with Mr. Hewitt's remarks regarding the necessity of paying due regard to the surface condition over which the composition is to be applied when formulating an anti-corrosive composition and particularly when deciding on its pigment/binder ratio. As he states, a different ratio may prove desirable when repainting old plates that carry a previous and presumably porous paint film than when compositions are applied to a new unpainted hull.

(4) Leaching-rate determinations were made at the time on anti-fouling composition AF 10/43 and we are indebted to Mr. K. A. Pyefinch for the following statement of the results :

Test Conditions.—The composition was tested 18 days after milling. An area of 2 sq. in. of slide face was painted, the paint being applied directly to the ground-glass surface.

Painted and Immersed : 18.11.43. Sea-stored slides.

Leaching Rates Observed, microgrammes/sq. cm./day.

Days after Immersion.	Temp., °C.	Leaching Rates, Cu.
4	?	15.9
12	13.7	15.5
29	13.0	4.5 *
61	15.5	10.5
126	18.3	15.3
243	16.7	9.8

* This value is probably incorrect.

† *Transactions of the Institution of Naval Architects*, 1946, vol. 88, p. 240.

(5) We are in complete agreement with Mr. Hewitt, and have repeatedly emphasized this in the past, that ships' bottom and indeed all painting schemes should be considered and tested as a whole. In this connection, it is particularly necessary that studies on anti-fouling compositions should proceed *pari passu* with those on anti-corrosive compositions.

(6) Reference to successful service tests on anti-corrosive composition No. 173 will be found in the paper by Professor J. E. Harris and W. A. D. Forbes †. The further statement by the latter made subsequent to Mr. Hewitt's own contribution, namely, that "The Admiralty has tried out paint No. 173 on a very large scale and found it very satisfactory" should be a final and satisfactory answer to his enquiry but, as a matter of interest, we may add a few details of results of service tests that have become available since we have submitted our paper.

By arrangement with the Director of Merchant Shipbuilding, full-scale service tests were made on the bottom of a new oil tanker, which was painted in quarters, as to one half with formulated anti-corrosive paints and anti-fouling compositions developed as a result of the Marine Corrosion Subcommittee's researches and as to the other half with proprietary compositions supplied by a member of the Association of Ships' Compositions Manufacturers. Two coats of anti-corrosive composition were applied whilst the vessel was on the stocks and a further anti-corrosive coat plus a finishing anti-fouling coat in dry-dock after fitting out. The vessel then saw service with the Admiralty as a Royal Fleet Auxiliary, going out to the Far East. The bottom was carefully inspected on dry-docking at Bombay, 11 months later, when the Captain Superintendent, H.M.I. Dockyard, Bombay, reported that the entire hull was heavily fouled and that there was nothing to choose between the formulated anti-fouling composition and the proprietary material; this was perhaps not surprising after such a period at sea, the greater part of which was spent in tropical waters. On the other hand, as regards the protective properties of the painting schemes, the advantage was with the Marine Corrosion Sub-

Committee's paints, as will be evident from the following results of the inspection at Bombay :

Percentage Area of Bottom—	M.O.S.C., Painting Scheme,	Proprietary Painting Scheme,
Devoid of paint or rusted .	9	16
Stained with rust . . .	26	49
Perfectly intact paint . .	65	35

The anti-corrosive composition used in the Sub-Committee's painting scheme was No. 173. It should be added that the manufacturers of the proprietary painting scheme took part in the trial in a very co-operative spirit and were aware of the conditions of the test.

(7) As Dr. Mayne points out, the order of merit of the media tested by us corresponds roughly with their relative resistance to saponification and hydrolysis, and we are in general agreement with his views. Our present attitude towards the subject may briefly be stated thus :

In the case of media not primarily suitable for the formulation of anti-corrosive compositions owing to the relative ease with which they may be saponified and hydrolysed by sea-water and/or the cathodic-reaction products resulting from electrolytic corrosion of the steel hull beneath the paint film, of which type of medium an ordinary linseed-oil medium is a good example, the pigmentation of the composition may play a major part in determining the protective performance of the paint film. It is probably fair to state that in pre-war days many compositions were of this type, *i.e.*, were formulated with non-suitable media, with the result that great practical importance became attached to the correct choice of pigmentation. We are not clear, however, as to how far differences in pigmentation are of crucial importance when the anti-corrosive composition is bound with a water-resistant non-saponifiable medium, and further researches are necessary to clarify this point. In general, we think it probable that the use of a suitably chosen inhibitive pigment, such as basic lead sulphate, will prove advantageous even in the better and more resistant media that are now being developed as a result both of the Marine Corrosion Sub-Committee's researches and of investigations within the ships' bottom composition industry itself. We may add that many of our views on these and other fundamental matters are in consonance with those expressed by G. Dechaux, whose paper * on the subject will repay study.

(8) We appreciate Mr. Forbes' kind reference to the service value of composition No. 173, as determined by Admiralty trials. We are particularly glad to have his statement regarding this, which we have already quoted, because in the early stages of our researches, the work was

subjected in some quarters to a certain amount of criticism, which did not always appear to be advanced in a constructive or impartial spirit; † this simple statement by Mr. Forbes is by far the best reply to make to this.

(9) We agree with Mr. LeBrocq that the relative behaviour of different pigments of the zinc chromate family may be influenced to a major degree by their content of water-soluble compounds and will, therefore, differ according to their mode of preparation and chemical constitution. Clearly, however, it would be unwise to discuss this subject in greater detail on the basis of the comparatively few tests reported in our paper.

(10) As we stated in the text, we regard the beneficial action of basic lead sulphate in the anti-corrosive paint films tested by us as being associated with the gradual and progressive formation of lead soaps. We cannot claim that the fundamental principles involved are clearly understood at present and, having regard to their more fundamental studies in this problem, we look to Dr. U. R. Evans, Dr. J. E. O. Mayne, and other workers in this field to establish these in due course.

(11) When the International Paint and Compositions Co., Ltd., refer to the application of a definite weight of paint per unit area, we presume they mean that all compositions tested should be applied at uniform thickness (the application of a constant weight of paint per unit area would not necessarily ensure uniformity of film thickness in the case of a number of compositions differing widely in specific gravity and in volatile content, as in that of the tests under discussion). We are in general agreement with this principle and have subscribed to it so far as is practicable in researches of this type. It is only fair, however, to point out that some variation in film thickness as between different compositions is inevitable and would correspond more closely to practice than strict adherence to standard film thickness. Moreover, the complications introduced into the physical preparation of the specimens by too rigid an insistence on uniformity in this respect would defeat its own object by introducing other variables.

(12) We have no wish to rekindle old controversies and it is perhaps arguable that the comparison with a proprietary painting scheme might have been better omitted. On the other hand, in view of the earlier criticism of our work, to which we have already referred, we felt it desirable to attempt to give the general reader with no specialized knowledge in this field, a clear-cut indication of the relative merits of the compositions we have developed. It should be noted that we were at pains to point out in the

* G. Dechaux, *Peintures, Pigments, Vernis*, 1942, vol. 17, pp. 254, 732, and 758.

† See "Paint Manufacture," July, 1944.

text that the proprietary painting scheme was at a disadvantage as regards film thickness, but we will now add what we omitted to state then, namely, that it is improbable that any increase in film thickness within reason would have rendered its performance comparable with that of the system based on our anti-corrosive composition No. 173.

(13) Whilst we agree that painting over bare steel and painting over old paint are different problems, and are aware that there is a growing practice for some manufacturers to supply different compositions for the two purposes, we did not find in cases where alternative primers for bare steel were supplied in our earlier tests, that this invariably led to an improvement as compared with the ordinary scheme of the same make.

(14) The necessary data to work out the film thickness of the proprietary painting schemes referred to in section D(1) (b) of our paper are not available, but we concede that judging by the weights of the dry paint films the advantage may lie, in general, with our formulated schemes in this respect. The argument cannot, however, be used both ways, because tests were made both on new and on old painted steel plates and in the latter case, at least, no alteration would normally have been made by the manufacturers in the consistencies of the compositions used.

(15) The Company seem to have been unfortunate in their experience with anti-corrosive composition No. 173. As we report in the present paper, we have observed reasonably good results with it in our own raft tests. Dr. Wormwell, in his verbal contribution to the discussion states that "accelerated tests with the C.R.L. high-speed rotor apparatus at Teddington confirm the good quality of paint No. 173 in regard to adhesion and freedom from serious flaking and blistering under conditions of rapidly moving, well-aerated seawater. Indeed, the resistance of this paint is such that laboratory tests of a still greater degree of acceleration will be necessary if the period of test is to be reduced below fifty days." Further, as we have already noted, Mr. Forbes has voiced the Admiralty's satisfaction with anti-corrosive composition No. 173 as regards service behaviour itself. As a matter of fact, we can even remove the fresh-water bogey because it so happens that, in response to a request from Dr. G. S. Baker, a formulated anti-corrosive paint for underwater use, essentially similar in formulation to that of paint No. 32, the prototype of anti-corrosive composition No. 173, was supplied for the repainting of the wavebreaker of the Froud tank at the National Physical Laboratory. We are permitted to state that this painting scheme has given entire satisfaction under those conditions of immersion in fresh water.

(16) There might be some substance in the

contention that the weighting factor of 1 for blistering as compared with 10 for rusting fails to give adequate importance to the former type of defect, if our assessment of the performance of the painting schemes were based solely on the index figure observed during the periodical raft inspections at the exposure site. It should be recalled, however, that the index figure is but one of some half-dozen observations entering into our final survey of the results, and that any serious blistering of the type described by the Company would have a seriously adverse effect in several respects on the compositions concerned, because the paint film would be detached at the blistered areas by the cleaning prior to the final laboratory examination. The loss in weight recorded would be affected thereby and the percentage area of intact paint would also be reduced; both these factors are taken into account in the final assessment.

(17) We thank M. Mardonie for his appreciative remarks, which call for no reply save we should like to stress that our statement regarding the greater degree of blistering on the pickled and weathered specimens as compared with the as-rolled and weathered ones should not be misunderstood. This blistering is of the fine pin-head type and, on electrochemical grounds, we should anticipate that larger blisters, much more serious in their practical effect, would be more likely to be produced on steel still carrying mill scale than on descaled steel, although the total area of the blisters might be less.

(18) We should make it clear in reply to Mr. Jones that it is not the practice of our colleagues responsible for the actual evaluation of the test surfaces, to record results to the nearest 1%. We have a standard scale of permissible returns, such as 0%, 0.1%, 0.2%, 0.5%, 1%, 2%, 5%, 10%, &c., in which the individual assessments are capable of easy differentiation; intermediate values are not returned. We agree that there would be no point in endeavouring to distinguish between, say, 30 or 31% of rusting. In such cases the figure would be rounded off to the nearest standard return.

(19) We have already discussed the question of the weighting factors adopted for blistering, flaking, and rusting; obviously, there is nothing sacrosanct about the figures 1, 2, and 10 that we have adopted. Although these represent our views of the relative importance of these three factors, we should not be disposed to quarrel with others who might think otherwise. We maintain, however, that the index figure, as calculated by us, is a useful concept and has considerable practical value if interpreted with a reasonable degree of caution.

(20) We are a little surprised at Mr. Jones' inability to detect fine blisters on paint films applied over rusted areas, but it is possible that in cases

where tests were made on relatively thin panels thoroughly cleaned by wire-brushing, the quantity of rust left on the surface would be so small as to reduce the degree of blistering to such an extent as not to be readily detectable, particularly if fouling were present on the surface as well. Nevertheless, this tendency for fine blistering is a fundamental and inseparable concomitant of the chemical nature of the rust.

(21) Mr. Jones' remarks about the spreading rate has already been largely answered in dealing with the contribution of the International Paint and Compositions Co., Ltd. He seems to have misunderstood the purpose of our final adjustment of the consistency of the paint, which is to produce a paint with such properties of flow under the brush as to be readily acceptable to a practical painter as suitable for hand-application. There is undoubtedly a natural spreading rate or, more precisely, a comparatively narrow range of spreading rates within which this state of affairs will obtain and which will not in general be the same for compositions of different formulations and characteristics.

(22) There is a good deal to be said for Mr. Jones' statistical analysis of our results and there can be no doubt of the value of this method of approach. We do not propose, however, to follow him in detail because, after all, his main conclusion is that certain of our results must be taken with caution, a fact to which we ourselves have already alluded. We might perhaps point out, with reference to the analysis of the zinc oxide group of compositions shown in Fig. 6 and Mr. Jones' Tables A and B, that the behaviour of most of the compositions concerned in his analysis was so poor that it might be considered a sheer waste of good mathematics to endeavour to distinguish between them. We see no reason to change our views regarding the relative merits of zinc tetrahydroxy-chromate and zinc chromate, on the one hand, or of the relative values of media *A* and *B*, respectively, for use with zinc oxide on the other, subject to such limitations as we ourselves have expressed in the text. In the first case (see Fig. 3), out of five comparable paints, all five were graded as bad when pigmented with zinc tetrahydroxy-chromate, whereas two were graded as moderate when pigmented with zinc chromate. Similarly, of four comparable pairs of paints, all of them in medium *A* were classed as bad, whereas two in medium *B* were classed as moderate.

(23) We attach more weight to Mr. Jones' analysis of basic lead sulphate series and are much indebted to him for this. We hope that additional evidence as to the correctness or otherwise of his views will become available as a result of further experimental work that is now being planned.

(24) We thank Mr. Truelove for his kind remarks and would assure him that we are fully conscious

of the practical difficulties encountered by compositions manufacturers, both during the war and at present, with reference to the supply of suitable raw materials. It is, at least in our view, the primary function of research to assist industry to new and better methods, and we see no reason, now that collaboration has been established between the Marine Corrosion Sub-Committee and the branch of the paint industry responsible for the production of ships' compositions, why considerable practical progress should not ensue as a result of joint investigations; this collaboration has already led to a more sympathetic understanding by both sides of the others' difficulties and points of view.

(25) Finally, in reply to Mr. Truelove's question regarding Burntisland red, the material used in our tests was a specially prepared material from which water-soluble matter and alkali had been eliminated.

Professor HARRIS replied: Dr. Wormwell's comments on the work are much appreciated; Dr. Vernon and he have both contributed substantially to the investigations.

Cases have occasionally been reported where a growing barnacle has chiselled into a soft paint coating, removing the paint down to the bare metal. If a vessel fouled in this manner suffers heavy scouring, the barnacle shell may be abraded by the process and the exposed bare steel surface will undoubtedly suffer subsequent corrosion. So long as the barnacle is not removed completely, however, we have no evidence that it encourages corrosion in the manner described, but it is hoped that Mr. Butlin may be able to provide further evidence on this point. Reference is made in the first report to a statistical analysis of a simple test-panel experiment to determine the time sequence of corrosion and fouling. Ample evidence of corrosion being followed by fouling was obtained, as might be expected, but no evidence of the reverse process was observed. A system with very inferior powers of adhesion would of course tend to be completely stripped if fouling settled and were subsequently torn off—but there is no reason to believe that this state of affairs occurs more than very rarely in practice.

Mr. D. H. Hewitt refers to the question of treating the anti-corrosive and anti-fouling coating as part of a single system; this is a point which the Marine Corrosion Sub-Committee has always stressed. To reduce the interaction between the two coatings to a minimum, it is absolutely essential that the anti-corrosive coating should dry as completely as possible so as to prevent "bleeding" into the anti-fouling layer. So far as possible, service tests are always designed to investigate the capabilities of a complete paint system rather than of one of its components.

Mr. W. A. D. Forbes is justified in suggesting that a more rigorous and detailed treatment of leaching curves is required. The present Report is seriously out-of-date owing to delays both in presentation and in publication; later reports will add a great deal to the information given above. A particularly profitable change in technique has been the immersion of compositions in an actual tide-way through the whole period of their storage, a matter of some technical difficulty where tidal rise and fall is very great, but which has presented no problem to the American investigators, who immerse their leaching slides from a pontoon in the harbour of Woods Hole. The need for a standardized method of measuring leaching rates is very great and the efforts of the Leaching Rate Panel are largely directed to this end. It will be realized that in the present anti-fouling report we have been more concerned with a fundamental study in the formulation and success of experimental compositions; for this purpose standardization is not a material factor, provided that the tests are carried out under strictly reproducible conditions. It would have been quite impracticable to use in the present studies the methods suggested by the Leaching Rate Panel, since neither the space nor the facilities were available for carrying out the tens of thousands of leaching determinations which have been made by the simpler method on these small experimental slides.

Mr. Forbes' suggestion that more rapid breakdown should occur at the after end of the ship is a point well worth investigating in practice, but we have no data on the subject at present, though there is a general impression that this is true.

The fact that the Report gives little guidance in the formulation of anti-fouling paints from the point of view of the actual material to be used is again due to the early period to which it refers; later reports will soon be available and will provide useful information on this point. The soluble type of matrix is on the whole the best proposition for general use, but there are cases where the composition is subjected to severe erosion in which an insoluble and physically very resistant matrix is desirable; in such cases contact leaching provides a practicable alternative. There is some evidence that with a soluble matrix the leaching rate when the ship is in port, immediately after a period at sea, is higher than that in a raft test, the paint thus providing rather better protection than the raft or laboratory experiments would suggest; Mr. Forbes is probably correct in saying that the reverse may be true for paints of the contact-leaching type.

The question of laboratory tests under moving-water conditions is a most important one and such tests are already being carried out on a small scale; it is hoped to increase the facilities

for this work as soon as the apparatus can be provided.

Dr. G. S. Baker's estimate of the depth of the sub-laminar layer is a most valuable contribution. It is only necessary to add that in view of the existence of this layer the diffusion of poisons from the surface of the paint, even at relatively high water speeds, will be primarily controlled by a simple concentration gradient. At the same time, there will be a reduction of the concentration in the deeper layers as a secondary effect of the rapid water flow.

The comments of the International Paint and Compositions Co., Ltd., are very much welcomed as a careful and stimulating contribution to the discussion. With regard to the statement on p. 315 P, the author's view-point is that every effort must be made to persuade shipowners that it is worth their while to invest in compositions of a very much greater degree of effectiveness than those in use at present. It is certain that many composition manufacturers are in a position to produce these better coatings, and it is unfortunate that data do not at present exist to indicate the exact financial loss suffered through the use of compositions which, while not regarded as inferior in comparison with accepted standards, are definitely so in comparison with the standards which can be, and ought to be, attained from the point of view of the most efficient working of the ship. In suggesting that too much emphasis has been placed by users on the cheapness of a composition, the author feels that he would be strongly supported by the composition manufacturers.

The toxicity experiments were done with extreme care, and controls showed clearly that the organisms could survive for many times the 6-hr. period in natural sea-water. However unbelievable the figures appear, they are based on carefully replicated experiments, though admittedly on a non-fouling organism. The effect of the anion on toxicity in sea-water solutions is very great indeed.

This is not to say that these differences may not disappear when the same poisons are used in paint. It is evident that the loss of poison from the painted surface does not necessarily take place in the form in which it has been added to the paint; copper, for example, is leached out either in the ionic form or in combination with chloride, and not as oxide, arsenite, thiocyanate, &c., as it exists in the pigment. Therefore, assuming the reliability of the toxicity values obtained by these laboratory tests, they provide, in fact, excellent evidence that all such paints function by release of toxic copper in the same form.

The fact that arsenite is highly toxic in sea-water but more or less ineffective in an anti-fouling composition is readily explained by the assumption that the arsenite radical does not pass

out as such into the sea-water under exposure conditions; oxidation to non-poisonous arsenate is an obvious possibility.

The suggestion that phenyl mercury acetate and nitrate both form the less soluble chloride in sea-water may be true for high concentrations of these compounds, but it is not necessarily so at the low values achieved at the surface of anti-fouling paint. Even if it is assumed that the phenyl mercury radical is the actual toxic agent inside the organism, it must at the same time be realized that the rate of passage of the poison into the organism is determined by the whole molecule and that therefore the time taken to kill the organism may differ very considerably between, *e.g.*, the complex acetate and the complex nitrate. The fact that most materials penetrate cells in an undissociated form is well known in biological work. An instance is found in the toxic effect of acids, which is greater for weak acids than for strong ones at the same *pH*.

The meaning of "a solution" of copper sulphate of a concentration of 1 in 40,000 in sea-water is certainly a little difficult to establish. What is undoubtedly true is that the toxicity of sea-water containing copper sulphate rises with the amount of copper sulphate added in a regular manner up to very high concentrations, well above those at which the solubility product is exceeded. It is known, however, that diatoms derive their iron from the colloidal iron in the sea-water, since the quantity of Fe^{II} and Fe^{III} ions available is far too small to provide the amount required. Our evidence would suggest that some similar mechanism may be involved in the toxic action of copper and that, while it is true that a concentration of copper sulphate of 1 in 40,000 does not indicate true solution, it has a definite quantitative meaning in these toxicity measurements.

The determination of the time taken to kill 100% of a culture of test organisms is not regarded by pharmacologists as a very sound basis for estimating toxicities; it is a standard practice to use the 50% death point, since this largely eliminates the very wide variability between individual organisms which is otherwise a source of error. At the same time, it is not necessary to assume that there is any serious discrepancy in experimental methods to account for the very different toxicity of mercuric chloride to this organism (*Nitocra spinipes*) and to those used by the International Paint and Composition Company's investigators. Differences of this order have been obtained by our own investigators in recent tests on a range of different types of organisms; even the same organism in waters of different salinity gives very different toxicity values for both copper and mercury, and it is not likely that the sensitivity of all copepods is the same.

Insofar as the remarks made on the leaching-rate determinations refer to the report on anti-fouling work, the following points may be noted. On many occasions tests have been made to see how far the leaching graph is linear over the range of the experimental period; although it is true that there was a falling-off at high copper concentrations, it was not a serious source of error up to concentrations even as high as $1\text{ }\mu\text{g./ml.}$ The much greater departures given by the International Paint and Composition Co., Ltd., may arise from the use of much lower rates of stirring.

It should be emphasized that the aim of the leaching test is to provide a laboratory tool for the investigation of compositions. Whether the test in fact imitates the normal conditions is of less importance than its value as a means of indicating the behaviour of the paint in the sea; from this point of view the experimental technique used at Millport was satisfactory. This is not to say that even higher temperatures or leaching methods dependent on other modes of breakdown, *e.g.*, in alkaline sea-water, might not be equally diagnostic and might indeed have considerable advantages from the point of view of analytical technique. The proof of the test lies in its ability to predict performance, not in its reproduction of the "normal conditions" of exposure of the paint.

Leaching experiments in normal sea-water have not revealed any significant change in *pH* during the experiment; the main effect of any variation in *pH* is on the rate of solution not of Cu_2O , but of the varnish matrix which, for a normal anti-fouling composition, governs the actual amount of Cu_2O available for solution.

The emphasis on storage conditions is completely justified and we are in full agreement with it. The most reliable method of carrying out leaching determinations is certainly to store the films in the sea and to carry out the leaching test immediately the specimens have been brought into the laboratory. Results thus obtained are at present far more reproducible than under any other conditions of laboratory storage of the films. For inland laboratories with no ready access to large quantities of pure sea-water, it is possible that use of an equivalent sodium chloride solution would provide an adequate substitute, since the leaching phenomena appear to be unaffected by the other constituents of sea-water.

The adsorption of copper on glass and other surfaces in the leaching bath is a matter which caused some difficulty in the early stages of the tests at Millport, but most of this has been overcome by scrupulous cleaning of glassware with chromic-acid/sulphuric-acid solution, followed by careful washing in tap-water and distilled water on every occasion before a leaching test is carried out. The leaching solution does not come into contact with any surface other than these cleaned

glass surfaces in the process and no difficulty has been encountered. An exception occurs where slides have been stored in the sea and have become heavily fouled; the organic matter on the slide may then take up considerable quantities of copper from the leaching bath. This is one objection to the storage of slides in the open sea, since compositions with a low leaching rate foul under such circumstances. For this reason, and also for the convenience of laboratories remote from the sea, it is highly desirable that some form of standardized leaching test should be devised which would make use of adequate and continually renewed saline solution in the storage tank.

The contribution of Mr. Crisp and Mr. Jones is a valuable essay in constructive criticism with which it is difficult to deal adequately in a small space.

The presentation in a scientific paper of results of raft tests is, as the writers suggest, a very difficult problem. Whilst emphasis has been laid on the qualitative rather than the quantitative criteria on which anti-fouling formulations are judged, this is not to say that we have taken no account of quantitative estimations or of regular and periodic assessment in order to trace the history of development of fouling. The paper by K. A. Pyefinch* on "Methods of Assessment of Anti-Fouling Compositions" is an indication of the detail in which fouling records are kept for every specimen exposed—the problem is much more one of a convincing *presentation* of such results in a short compass than of devising satisfactory criteria themselves.

It should be pointed out that in an experiment of type (1), where one or more factors of a basic formulation are varied, the very fact that this variation is accomplished in a series of definite graded steps itself increases the validity of the deductions, which will be based—not on the observations of duplicate specimens of one formulation—but on the analysis of variation in fouling over the whole range of (say) 72 specimens forming duplicates of a regular sequence of compositions.

The comparison of paints of widely differing formulations is of course another matter. So far as complete painting systems are concerned, variation is much more commonly encountered in the form of wide differences in the protective properties of the system (with concomitant influences on the fouling) than in the anti-fouling properties. In simpler terms, it is often easier to obtain significant and reproducible differences between a series of widely different anti-fouling coatings tested over one and the same protective coating than it is where the whole system is varied. Usually, however, the performance differences

between compositions *A* and *B* are of a different order than are differences observed between, say, *A* with 10% Cu₂O and *A* with 15% Cu₂O; in practice, though tests involving quadruplicate exposures (and even more frequent replication) have often been carried out, comparison between formulations can usually be satisfactorily accomplished in tests on duplicates.

The assessment of test panels is in practice carried out by an observation of the quantity (as a visual estimate) of each different fouling species at regular monthly intervals. This gives a very complete picture of the fouling process; the reproducibility of histories of duplicate panels is extraordinarily good.

The method of calculating the anti-fouling "lives" of paints is indicated in some detail in the paper by K. A. Pyefinch already referred to. The fact that the life is given to the nearest day is not intended to suggest that the test is reproducible to any such accuracy. Assessments being made at roughly 4-weekly intervals, the time at which a certain stage of breakdown is recorded will be estimated to about half this period—even with duplicate or triplicate exposures the mean will be subject to an error certainly of the order of 5–10 days. The greatest variability is in the type of fouling encountered, and it is questionable whether in the highly seasonal conditions around the British Isles it is possible to achieve any greater accuracy in an estimate of anti-fouling lives.

The use of a standard formulation prepared and exposed at the same time as a series of experimental paints is an obvious and useful suggestion. Since 1944 such controls have been developed, but it will be appreciated that the assessment of their reproducibility under varying conditions of exposure is itself a long-term problem. At the risk of repetition one might say that to grade a series of compositions all exposed at the same time in a single raft test is a very simple matter; to produce an objective and reproducible standard of performance valid for any number of tests at different times of year under different exposure conditions is a problem of infinitely greater difficulty—we would not claim to have solved it yet.

The variation in "performance," both in raft and leaching tests, between the laboratory and large-scale batches of the Sub-Committee experimental paint referred to in the paper by Harris and Forbes† was so large as to be far outside the range of the greatest possible experimental error in assessments yet encountered. In point of fact the large-scale batch fouled immediately (at the first assessment); its leaching rate was of the order of 2.8 µg./sq. cm./day, whilst the laboratory batches had given a leaching rate of 16.3 µg./sq. cm./day, and a raft life estimated at >220 days.

* *Journal of The Iron and Steel Institute*, 1945, No. II., p. 229 P.

† *Transactions of the Institution of Naval Architects*, 1946, vol. 88, p. 240.

The author would fully agree with the contributors' remarks on the desirability of a greater knowledge of the factors responsible for the presence and absence of certain fouling forms at particular sites—it is a cogent reason for supporting the fullest possible investigation into the fundamental biology of fouling forms. A paper in preparation by Mr. K. A. Pyefinch will present this side of the work with particular reference to barnacle fouling at Millport—it is impossible without careful and detailed work over a period of years accurately to assess the factors at any particular site.

There is no doubt whatever that *B. balanoides* settles successfully and in enormous numbers on test panels exposed at Millport (and Caernarvon). This may conceivably be related to the water temperature—*B. balanoides* is known to be limited in its occurrence by slight differences in temperature; the surface water temperature at which Dr. Crisp and Mr. Jones were working may have been appreciably different from that at Millport and Caernarvon. It is a little surprising to find that they have not succeeded in confirming the evidence of the "border effect" so universally encountered at Millport and also reported by investigators in the United States.

The statement that the water layer *immediately* adjacent to the paint surface is at rest does not of course refer to the whole layer of laminar flow but is to be taken quite literally; it is agreed that the velocity gradient in the whole layer is highest at this point—and in fact, if the velocity at an infinitesimal distance from the paint surface is zero, the other statement must necessarily be true. The point which has been stressed (in the paper by Harris and Forbes (*loc. cit.*), but not in the present contribution) is that there is no "mechanical" transfer of the dissolved poison at right-angles to this layer, since the flow is perfectly streamline; any transfer which does occur will do so by the normal diffusion process which is characteristic of still water, provided that one is dealing with a sufficient toxic surface area for the various depths in the laminar layer to attain equilibrium with the more concentrated layers lying immediately beneath them. Outside this zone eddy diffusion will supervene, and the concentration will fall off rapidly.

A further quantitative treatment of the theory is highly desirable, and it is hoped to attempt this at a future date. Recent experiments have shown that it is possible to relate quantitatively the width of the border to the leaching rate of the paint, but the variability of the tidal flow on the raft presents a more difficult problem to interpret in quantitative terms.

No work has been carried out on the anti-fouling action of copper alloys, but we have been informed of other results similar to those of Laque

and Clapp quoted; further information on this point is much to be desired. It would, for instance, be exceedingly interesting to obtain estimates of the actual rate of loss of copper from such alloys into the sea-water during an exposure test, to see if the results agree with those of the leaching studies. We have been only too anxious to find exceptions to the correlation between leaching rates and anti-fouling performance; since if such a perfect correlation exists, the scope for anti-fouling composition formulation is strictly limited by the poison content and its rate of loss. All that can be said at this stage is that for a considerable number of different copper compounds, for an organic arsenical such as chlorphenarsazine, and even (with certain reservations owing to possible loss of mercury in some non-toxic form) for mercury compounds, no evidence has yet disproved the existence of such a correlation. On the other hand, there is no obvious connection between critical leaching rate, anti-fouling action, and toxicity in sea-water, which is surprising; this is a field in which further work would be well repaid.

It is only too clear that the work with organic poisons raises far more problems than it provides solutions. The scope for new work in this field is enormous, and is far beyond the present resources of the team of investigators. It was largely in the hope of drawing attention to the possibilities of such investigation that the section on organic poisons was incorporated into the present Report. It has been necessary to postpone further work on these lines in view of more urgent problems, but the present account at least serves to emphasize that there is a major field for future research here.

It might be possible to explain the different toxicities of different mercury compounds by suggesting that they are not dissociated in solution and that the rate of penetration of the undissociated compounds varies, *e.g.*, with the lipid solubility and molecular size of the compounds. Such an explanation, however, is more difficult to apply to copper salts which, except for a few compounds like copper aceto-acetate, should be fully dissociated in reasonably dilute solutions.

With regard to the differences in toxicity of the two thiuram monosulphides, this does not occur in solution in sea-water (toxicity 6.0 in both cases) and the difference between the performance of the two compounds in rosin-oil paint is in line with the suggestion that it is connected with their fat-solubility.

Whilst the defects of the paints in this series of experiments are readily admitted, it is difficult to agree with the writers that "none of the poisons represented should be ruled out entirely." Unless the type of medium employed is completely different from any of those at present in use, the employment of naphtha-soluble poisons of rela-

tively low toxicity would appear to be out of the question.

We now come to that part of Dr. Crisp and Mr. Jones' contribution dealing with leaching tests. Reference to the text accompanying Fig. 3 will show that the arbitrary units employed to grade the fouling do in fact correspond to *qualitative* differences in the type of fouling as suggested at the end of section II. (4). Of the compositions tested two with fouling ratings of 1 and 2 would have been considered unfouled by most normal anti-fouling tests; the leaching rate of 10 gives a slight but appreciable safety margin. It is agreed that it would have been desirable to have more paints at higher leaching rates, but the rates were quite unknown when the experiment started.

Fig. 5 is intended to show the relatively good correlation between *copper* leaching rate and fouling. If we eliminate from the diagram the four or five compositions with appreciable mercury leaching rates the correlation becomes even better—especially when one considers these results in conjunction with other data (including independent results of American investigators and of the Millport team) which suggest a critical leaching rate for mercury alone of 2 $\mu\text{g./sq. cm./day}$. The deductions which, with some caution, one might draw from the curve are:

(a) Leaching rates of mercury below 1 $\mu\text{g./sq. cm./day}$ do not affect the correlation between copper leaching rate and anti-fouling performance (a majority of the paints is in this category).

(b) For mercury leaching rates above 1 $\mu\text{g./sq. cm./day}$ the anti-fouling performance is generally better than would be expected from the copper leaching rate alone.

(c) If there is any relation between leaching rate and the rate of loss of poisons into the sea in a raft test—and much experimental evidence as well as common sense expectation supports this view—then the mercury in most of the compositions is not contributing as an anti-fouling poison to their performance. It may of course contribute by controlling the copper leaching rate, but this is another matter—a different paint without mercury but with the same copper leaching characteristics would perform equally well.

As it happens, Fig. 9 was obtained from a later series of paints which were carefully formulated and milled under conditions which gave excellent dispersion. It is characteristic of a large number of cuprous oxide paints *not* containing mercury, as a future paper will show.

In fact the relation between the mean leaching rate at 30–60 days and the fouling on the compositions shown in Fig. 5 is not unsatisfactory. If three compositions with high mercury leaching

rates are omitted (a proceeding justifiable on independent data) the correlation coefficient between copper leaching rate and fouling is — 0.90; including all compositions it is still — 0.75.

The author sees no reason for disagreeing with the statement quoted by the writers from the papers of Ketchum and others. A great deal of work more recent than that incorporated in the present Report has been carried out since 1944, and leaching curves over periods up to 6–12 months have not produced evidence which contradicts any of the major conclusions arrived at here. Even if, however, one were to accept as a lowest common denominator of agreement, Dr. Crisp and Mr. Jones' statement that "It is of course true that if a paint is unsatisfactory as regards leaching in the early stages of its life, then its later history is of little importance," a study of leaching characteristics would be amply justified, and 50% of the formulations in Fig. 5 would not be considered worth the trouble of a raft exposure.

Mr. Truelove does a considerable service to the anti-fouling problem by stressing the conditions under which paint is applied in the docks and the price which consumers are willing to pay for compositions.

It is agreed that the criterion of success in practice of an anti-fouling composition is the quantity of fouling developed—though not the *ultimate* quantity, which merely gives the most impressive picture from the shipowners' point of view—the amount developed *during the period of the voyage* is likely to be better related to the increased fuel consumption. The suggestion that *Enteromorpha* and barnacles follow long after the smaller organisms is untrue except for slime on a fairly toxic surface—the investigators do not regard slime as "fouling." The Clyde steamer referred to in section II. (4) had an appreciable growth of weed (including *Enteromorpha* and several other species) and its light fouling was not connected with the paints employed, which were completely useless. The fact that "the effective life of commercial anti-foulings is in practice far greater than the authors indicate" is true, but merely signifies that biologically heavy fouling conditions are not nearly so frequently met with as is commonly supposed. Control test patches of non-poisonous paint will often show, and have often shown, good "anti-fouling performance" if the amount of fouling at the end of the voyage is used as the only criterion!

Differences in leaching rate between static and moving-water conditions certainly need fuller investigation; this problem has received considerable attention since the work to which the present Report refers. As pointed out in the Report, however, fouling takes place on a ship under practically static conditions—and the statement that "it is obvious that these (leaching

tests) are far from having any practical application as yet" is completely unwarranted.

Between Mr. Truelove's claim that leaching-rate tests have been made "on films of thickness less than is common on ships" and the International Paint Company's comment that "the general application rate (is) . . . somewhat heavier than is thought . . . to compare with coatings in practice" the present work is obviously on firm ground!

To suggest that *Tubularia* is an unsuitable test organism since it is *much* more resistant to poisons (the *much* has been inserted and is not in the Report) is incorrect. Later work suggests that the difference in leaching rate for paints affording protection against *Tubularia* and against barnacles is that between 10 $\mu\text{g.}/\text{sq. cm.}/\text{day}$ and 8 $\mu\text{g.}/\text{sq. cm.}/\text{day}$ respectively. The former figure is, we feel, not too high a safety factor to provide in an anti-fouling composition. The tests in Fig. 5 were carried out late in the season when the only fouling forms available were a very small number of *Balanus crenatus*, a series of exceedingly sensitive forms like the polyzoa, &c., and the usual autumn settlement of *Tubularia*.

The fact that little importance is attached to diatom fouling from the point of view of a vessel in service is accepted in the Report, section II. (4). The attractive suggestion that the provision of a permanent slime film would obviate the need for poisons is unfortunately offset by the fact, brought out in the Report, that such bacterial films derive their nutriment from materials (*e.g.*, resins) leached out from the paint film, which would therefore be equally limited in its life.

The author is very willing to admit that successful compositions exist—those illustrated in the last row of the much-discussed Fig. 5 are typical examples—though the figure, as Dr. Crisp and Mr. Jones point out, gives no indication of the *life* of the paints studied.

The figures given in section II. (6) "Fouling of Ships" are actually quoted from the reports of a marine superintendent on the state of the vessels; a more detailed examination of the fouling forms present has been made and will be published in a later paper. In the absence of exact data on speed loss or increased fuel consumption in relation to amounts of fouling present, the distinction drawn between lightly fouled and fouled is largely a matter of opinion; it is however relevant to say that there is independent evidence that even so-called "negligible" fouling can produce increases in surface resistance of the order of 5%.

That the present leaching rate is not a greatly "accelerated" test is true; it is still true that as compared with an elaborate raft test or a still more lengthy and costly service test, it offers enormous advantages; criticism of the coating thickness has already been mentioned.

The data given on tests with organic compounds are exceedingly interesting; it might however be pointed out with some relevance that a 3-min. kill of 90% of nauplius larvae bears no obvious relationship to conditions obtaining in practice, where on a paint which is of a normal successful type larvae frequently settle and metamorphose over a period of 24 hr. before finally falling off and dying.

Many factors other than naphtha-solubility may enter into the successful performance of an organic compound as an anti-fouling poison; an obvious one is ease of oxidation, which is a particular case of the more general one—whether the compound passes out of the paint film in a form identical with that in which it was originally incorporated. The author would be the first to admit that much more work needs to be done before the action of organic poisons is understood.

The estimation of leaching rates by biological assay is a method of general applicability and of very great importance. Mr. Truelove is to be congratulated on publishing this first record of the successful use of this technique.

It is agreed that on certain undercoats, especially those of a bituminous nature and also when the undercoat is not fully dried-off, low leaching rates will be obtained. Not only must the whole system be considered in a final assay of performance by this test, but the conditions of application should also be imitated as closely as possible. The differences quoted by Mr. Truelove, however, if one eliminates the evidently unsuitable bituminous primer, do not appreciably affect the picture; we are evidently dealing here with a paint which will adequately prevent fouling but which is losing copper at a somewhat higher rate than is necessary for this purpose; it would presumably be worth while, particularly in the later stages of raft and service tests, to include similar formulations with somewhat lower leaching rates which might have a relatively longer life.

The possible effect of formalin on the composition is one which was realized at an early stage, but tests on unslimed compositions showed that it had no effect on the leaching rate.

That rates higher than 10 $\mu\text{g.}/\text{sq. cm.}/\text{day}$ loss of copper might be required if the surface is heavily coated with organic matter appears possible; it would be interesting to know if such conditions (deposition of organic matter together with the consequent inadequacy of a 10- $\mu\text{g.}$ leaching rate) are actually encountered in such waters.

In attempting to summarize the author's views on the points raised by the discussion it is relevant to stress that of all the possible methods of testing an anti-fouling composition, one of the most highly suspect is the one most used in practice—the examination of fouling on a ship painted with the composition. Comparative tests on one voyage on the same ship are obviously useful, but fouling is

highly variable in its incidence and may be removed in scouring ports; failure of the paint, on the other hand, may be correctly or incorrectly attributed to bad conditions of application. The raft test is obviously better since it provides for more continuous fouling conditions and a carefully controlled painting technique; but there is still room for an objective "laboratory" test which is not so subject to natural vagaries and subjective assessments. The leaching-rate test offers considerable possibilities in this direction; the major difficulty in its use is undoubtedly the provision of suitable conditions for the storage of the test specimens.

The author would like to conclude by acknowledging the very great value of this stimulating and critical discussion. In working towards the common aim of encouraging the use of compositions of the best possible performance, the present research team, the shipowners, and the composition manufacturers should profit greatly from the fullest possible exchange of information.

The JOINT TECHNICAL PANEL ON THE LEACHING RATE TEST wrote in reply:

AT/V Ratio.—The adoption of a fixed *AT/V* ratio is useful because it permits a constant factor to be employed for converting leachate concentrations in milligrammes per litre to leaching rates in terms of milligrammes per thousand square centimetres per day. There is no particular reason why the value of the ratio should equal 60, and it might be that another figure could be used with advantage, particularly for paints which have a high leaching rate. The problem however is intimately connected with the maximum concentration of copper in the leachate which can occur before the rate of solution is retarded by saturation. Opinions differ concerning the solubility of cuprous oxide from cuprous oxide compositions and of copper from other copper compounds used in the manufacture of anti-fouling paints, and until more information is available it is difficult to determine whether the concentration-time curve is linear up to the value of 0.5 mg./litre. Considerable evidence exists to support the view that for some proprietary compositions the rate of loss of copper is retarded before a concentration of 0.25 mg./litre is reached, and that above this concentration the curve is no longer linear. This would suggest that a lower value for the *AT/V* ratio could be adopted with advantage for certain classes of paints.

Temperature.—The present working temperature of 25° C. was chosen because of the simplicity of thermostatic control at a temperature which is always above ambient. It is recognized, however, that the sudden change from cold sea-water storage to 25° C. in the leaching bath is undesirable because of the resultant disturbance of any

equilibrium condition existing in the paint film, and that it may be desirable to minimize this effect by standardizing a compromise temperature for the leaching bath of, say, 15° C.

Hydrogen-Ion Concentration.—There is a considerable amount of evidence and theory to support the view that the solubility of cuprous oxide in sea-water is affected by hydrogen-ion concentration, but the data provided by Ferry and Carritt cannot be extended necessarily without further investigation to cuprous oxide contained in anti-fouling compositions. It is recognized that the *pH* of the water to be used in leaching should be standardized, and that it should be as close as possible to that which obtains in the storage water. Experience has shown that, during storage, natural sea-water undergoes considerable variation in *pH* by virtue of the biological communities contained therein. Such differences would markedly affect the solution of cuprous oxide from a paint film. It might therefore be advantageous to leach in a solution of commercially obtained sea-salt prepared from evaporated sea-water, or alternatively in a synthetic sea-water made from individual chemicals. The biological effect on *pH* would be eliminated by either of these methods.

Storage Conditions.—The Panel agree in general with the points raised by the International Paint and Compositions Co., Ltd.; the problem of storage, particularly as it affects inland stations, is the subject of present investigations by the Panel. No details were entered into in the Interim Statement, but it was thought that the brief warning regarding laboratory storage was advisable. While the necessity for storage-bath agitation is recognized, the degree of agitation normally required to overcome diffusion effects has not yet been fully determined, but it would appear to be low for those paints which have been studied. Experiments conducted by workers in the United States indicate that once diffusion-control of leaching has been overcome, further agitation of the storage medium has little effect, but a high degree of agitation is necessary to overcome diffusion effects when dealing with "contact-leaching" paints with a high pigment content. It seems desirable that inland laboratories conducting leaching in synthetic sea-water should carry out storage in the same medium.

Slime Removal.—The criticism of the use of formaldehyde to remove slime is legitimate, and has been realized by the members of the Panel. So far, no really satisfactory method for slime removal has been evolved. Even the careful use of a small brush may remove part of a chalking paint surface and give rise to a false leaching figure. On the other hand, recent experience has shown that little difference in leaching rate will be found between slime-coated and cleaned panels

unless the slime is excessive. In this case, it is probably sufficient to remove the grosser accumulations by a gentle stream of water.

Adsorption of Metallic Ions upon the Apparatus.—The addition of acid to leaching jars to dissolve copper which may be adsorbed on the walls of the apparatus is not to be recommended, as small flakes of paint dislodged by aeration-agitation would pass into solution and give rise to false figures. Absorption by the shellac-impregnated cork plate-holders of the leaching apparatus can be overcome by modifying the plate-holder.

Thickness of Paint Film.—The Panel agree that it is desirable to use approximately the same film thickness for leaching experiments as is normal for the coating of a ship's hull or panels for raft exposures.

Undercoats.—The remarks on the effect of undercoats on the leaching rate of anti-fouling compositions are of interest, but the experience so far of members of the Panel has been that the use of undercoats has little or no effect on the leaching rate.

THE ORIGIN AND CONSTITUTION OF CERTAIN NON-METALLIC INCLUSIONS IN STEEL.*

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(Figs. 4 to 85 = Plates XLV. to LVIII.)

SYNOPSIS.

The phase diagrams relating to the study of non-metallic inclusions in steel are reviewed and the important ternary system $MnO-Al_2O_3-SiO_2$ examined; the most probable phases occurring in the complex system $CaO-MgO-FeO-MnO-SiO_2-Al_2O_3$ are described in the light of the review. A large number of different types of inclusions in acid open-hearth and basic electric-furnace steels (direct-poured, tundish-poured, and bottom-poured) are identified by extraction and by the use of phase-diagram data, chemical analysis, metallographic examination, and X-ray examination.

It has been possible to ascertain the sources of many of these inclusions with a fair degree of accuracy, and a table summarizing these results is given.

Practical suggestions are made for reducing the incidence of harmful non-metallic inclusions in steel.

INTRODUCTION.

IN most steels the presence of non-metallic inclusions is undesirable, because they are often a potential source of weakness, whether the steel in which they occur is being stressed statically or dynamically. In addition, inclusions in steel are the cause of many rejections on mechanical testing, especially when the test-pieces are prepared transversely to the grain flow of the material. Such flaws are revealed mainly by the tensile test, the most sensitive property being elongation, although transverse Wöhler tests and transverse Izod tests may be equally discriminating. Inclusions occasionally lower the apparent maximum stress, because the stress concentration which their presence brings about causes premature fracture. The steel must therefore be clean if its maximum mechanical properties are to be achieved, *i.e.*, it should contain the minimum of non-metallic matter, in addition to being free from banding and segregation.

It is not difficult to demonstrate that steels tested transversely to the grain flow and containing roughly oval-shaped inclusions, either continuous or discontinuous and so dispersed that they lie normal or approximately normal to the lines of applied stress, are likely to lead to low mechanical properties. The most disturbing feature of non-metallic inclusions, however, is the uncertainty as to where and in what form they may appear; therefore any evidence regarding their constitution and source and how to eliminate that source is valuable.

The three main sources of non-metallic inclusions are :

- (1) Deoxidation, and the segregation of the products of deoxidation.
- (2) The presence of sulphur and phosphorus, and the segregation of their compounds.
- (3) Extraneous sources.

(1) Deoxidation is no doubt responsible for some unavoidable inclusions in steel. However, steel-melting and deoxidation techniques are now sufficiently well developed to enable large quantities of such inclusions to be avoided. Difficulties may, however, be encountered in large ingots and also in badly designed ingots, where segregation renders the deoxidation products much more harmful, while low casting temperatures will prevent the escape of many inclusions into the part of the ingot normally discarded. In the present paper attention will be focused on the effect of aluminium, which is widely used as a final deoxidant and for controlling grain-size, as its injudicious use can lead to a type of inclusion which is very troublesome in machining and drilling.

(2) The sulphur content of the finished metal can be controlled in all steelmaking processes. This is accomplished by special selection of the charge materials and the fuel, as in the acid process, or the sulphur (and phosphorus) can be partially removed by chemical methods, as in the basic process. Serious sulphur segregation or inclusions were encountered only on rare

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occasions during this investigation, and inclusions of this type will therefore be ignored.

(3) Although the formation of some non-metallic inclusions is inevitable in ridding the molten steel of its gaseous and soluble constituents by converting them into solid particles, there are many other sources which merit even more careful study. During production, molten steel and slag must come in contact with a large number of refractory materials, such as the furnace lining, the launder lining, the ladle lining, stoppers, and nozzles, tundish linings, and, in bottom-pouring, trumpets and runners. As a result of their erosion and corrosion by the molten slag and metal, these refractories offer a very real and ever-present source of non-metallic inclusions; evidence of such fluxing can be readily noticed on visual examination of the mentioned refractories after a heat of steel has passed over them. In addition to physical erosion, the slag chemically attacks the launder and ladle linings, and in the case of tilting furnaces (where the slag is allowed to pass into the ladle from the commencement of the tap) some of the slag and its reaction products may be trapped in the steel.

By far the larger number of inclusions and segregates found are of extraneous origin, and it is therefore with these inclusions that this paper is chiefly concerned. The term "inclusions of extraneous origin" covers all inclusions introduced into the steel as a result of:

- (a) The trapping of the slag.
- (b) The trapping of corroded and eroded refractories used at any stage in the steel-making.
- (c) The trapping of the products of reactions between the steel and the refractories with which it comes in contact.

The possible sources of non-metallic inclusions originating from deoxidation and extraneous influences therefore cover a wide range. However, the constitution of these inclusions may have features which can be correlated with their origin. Since the establishment of the origin of the various non-metallic inclusions would be of material value to the steelmaker, the aim of the present investigation was to determine the constitution of these inclusions and to establish, where possible, characteristic features in the constitution which might be indicative of their origin.

The first stage is the consideration of the phase diagrams of the relevant oxide systems. The chief oxides occurring in inclusions are:

- (1) Deoxidation products: FeO, MnO, SiO₂, and Al₂O₃.
- (2) Acid open-hearth slag constituents: SiO₂ (about 50%), FeO, MnO, and CaO (less than 10%).

(3) Basic-electric finishing slag constituents: CaO and SiO₂, usually as 2CaO.SiO₂, with MgO (less than 10%).

(4) Products of reaction between basic-electric slag and firebrick: CaO, SiO₂, Al₂O₃, and small amounts of MgO.

(5) Products of reaction between manganese of steel and firebrick: MnO, SiO₂, Al₂O₃, and small amounts of FeO.

A knowledge of the phase combinations of MnO, FeO, SiO₂, and Al₂O₃, and of parts of the more complex systems containing CaO and MgO, is required for the determination of the constitution of the above types of non-metallic inclusions. A study of the very comprehensive review of the constitution of acid and basic open-hearth furnace slags by White¹ reveals that much of the necessary phase data is not available; but, with additional knowledge of the ternary system MnO-Al₂O₃-SiO₂, sufficient data for the elucidation of the constitution of extraneous non-metallic inclusions may be deduced. Furthermore, according to Rait,² the inclusions produced by the reaction of manganese in liquid steel with firebrick consist chiefly of MnO, Al₂O₃, and SiO₂; these are among the most frequently occurring types of inclusion and are very detrimental to the transverse mechanical properties of the steel. Hence a knowledge of the system MnO-Al₂O₃-SiO₂ is essential for the identification of such inclusions in steel.

THE SYSTEM MnO-AL₂O₃-SiO₂.

Although Herty,³ Wentrup,⁴ and Glaser⁵ have published some data on MnO-Al₂O₃-SiO₂ melts, and Hay⁶ has proposed a tentative liquidus diagram, the system has not been thoroughly established, and accordingly an investigation was commenced. However, during the initial stages of this investigation, Snow⁷ published the results of a systematic examination of the equilibrium relationships at the liquidus surface of part of the MnO-Al₂O₃-SiO₂ system, and so it was thought that a less comprehensive investigation of the system, using the X-ray powder method of identification of the crystalline phases in contrast to the petrographic methods chiefly used by Snow, would provide a useful and sufficient check. Furthermore, the examination of polished synthetic-slag sections was required for comparison with the inclusions in the various steels, and, since many of the samples had been heat-treated at temperatures lower than the liquidus temperatures in Snow's diagram, it was also necessary to examine synthetic-slag samples which had been melted and subsequently annealed at the lower temperatures.

The three bounding binary systems are MnO-SiO₂,⁸ MnO-Al₂O₃,⁹ and Al₂O₃-SiO₂.¹⁰

In the MnO-SiO₂ system there is a eutectic at

1208° C. between the two incongruent melting compounds tephroite ($2\text{MnO} \cdot \text{SiO}_2$) and rhodonite ($\text{MnO} \cdot \text{SiO}_2$). Tephroite is a member of the isomorphous orthorhombic olivine group of minerals which includes fayalite ($2\text{FeO} \cdot \text{SiO}_2$) and forsterite ($2\text{MgO} \cdot \text{SiO}_2$); rhodonite is triclinic and belongs to the pyroxene group of minerals. A notable feature of the system is the occurrence of a range of immiscibility in the liquid state at high silica contents, owing to the fact that liquid SiO_2 and the liquid silicates are only partially soluble in each other, even at steelmaking temperatures. The $\text{CaO}-\text{SiO}_2$ ^{11, 12, 13} and $\text{FeO}-\text{SiO}_2$ ^{14, 15, 16} systems are characterized by similar immiscibility ranges. The fluxing powers of the basic oxides for solid SiO_2 vary inversely as the distance of this portion of the liquidus from the SiO_2 end of the diagram. The tridymite-cristobalite transformation is indicated on the diagram by the horizontal broken line at 1470° C.; above this temperature SiO_2 crystallizes from the melts as cristobalite, below it as tridymite.

There is one compound in the $\text{MnO}-\text{Al}_2\text{O}_3$ system, namely, galaxite ($\text{MnO} \cdot \text{Al}_2\text{O}_3$), which belongs to the cubic spinel group of minerals. It melts incongruently at 1560° C., and forms a eutectic with MnO at 1520° C. The characteristic property that spinels possess of forming solid solutions with excess Al_2O_3 and Fe_2O_3 is illustrated in this system. The property is attributed to the fact that Al_2O_3 and Fe_2O_3 can exist in the γ form as well as in the α or rhombohedral form; the γ form has the spinel structure.

Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), which melts incongruently at 1810° C., is the only binary compound in the $\text{Al}_2\text{O}_3-\text{SiO}_2$ system. It forms a eutectic with SiO_2 at 5% SiO_2 and 1545° C. Unlike the $\text{MnO}-\text{SiO}_2$ system, this system has no liquid-immiscibility gap at the SiO_2 end. Mullite is orthorhombic, usually crystallizing from glass as very fine anisotropic needles.

Summary of the Data due to Snow.⁷

The equilibrium relationships are shown in Fig. 1, and the isotherms in Fig. 2. Two ternary phases, namely, $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ and $2\text{MnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, have a range of stability on the liquidus surface. Spessartite ($3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) was shown by the X-ray powder method to have the same structure as natural garnet; it crystallizes in the form of dodecahedrons and occasionally as trapezohedrons. Small crystals had the appearance of spheres, but octahedrons were not present. It is isotropic, pale green, and has a refractive index of 1.810 ± 0.005 . It has a low melting field in the centre of the system and can coexist with all but two of the phases which are stable in the system, the exceptions being MnO and mullite. Spessartite probably has a congruent melting point of $1200^\circ \pm 5^\circ \text{C}$.

$2\text{MnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ has an atomic structure similar to cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$), according to X-ray data. The crystals are optically negative, probably slightly biaxial, with parallel extinction and negative elongation, and many show a hexagonal cross-section. The refractive

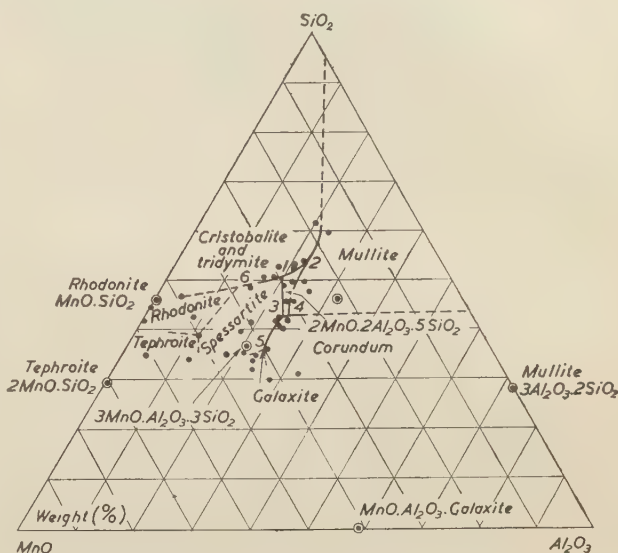


FIG. 1.—Equilibrium Diagram of part of $\text{MnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ System (according to Snow⁷).

indices for the α - and γ -rays are 1.537 and 1.558 respectively. It has a very small field of stability at the liquidus surface and melts incongruently to form mullite and liquid at $1200^\circ \pm 10^\circ \text{C}$. This phase seldom crystallized during the initial cooling of a melt, because another anisotropic

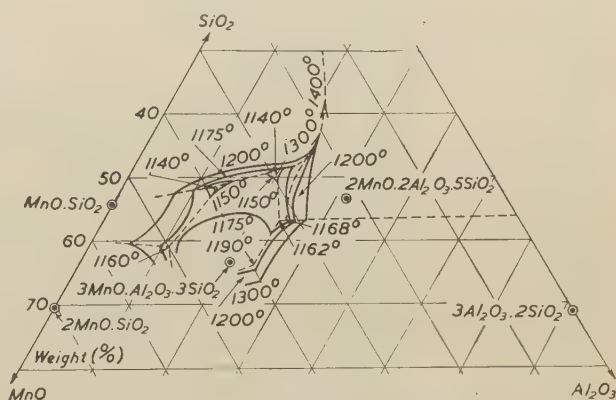


FIG. 2.—Isotherms ($^\circ \text{C}$.) in part of $\text{MnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ System (according to Snow⁷).

constituent, termed "extinction crystal," usually formed. These crystals had a high birefringence and an extinction angle of 43° . The α -ray had a refractive index of 1.605, and the γ -ray an index greater than 1.626; the third index was not investigated because the crystals occur as

TABLE I.—*Quintuple Points in the System MnO-Al₂O₃-SiO₂.*

Quintuple Point.	Phases.	Composition, %.			Type.	Temp., ° C.
		MnO.	Al ₂ O ₃ .	SiO ₂ .		
<i>Quintuple Points Established.</i>						
1	Spessartite, tridymite, 2MnO.2Al ₂ O ₃ .5SiO ₂ .	30	19	51	Eutectic	1140 ± 10
2	Tridymite, mullite, 2MnO.2Al ₂ O ₃ .5SiO ₂ .	24	23	53	Peritectic	1200 ± 10
3	Spessartite, 2MnO.2Al ₂ O ₃ .5SiO ₂ , corundum.	33	24	43	"	1162 ± 5
4	2MnO.2Al ₂ O ₃ .5SiO ₂ , mullite, corundum.	32	25	43	"	1168 ± 5
5	Spessartite, corundum, galaxite.	40	24	36	"	1190 ± 5
<i>Quintuple Points Indicated.</i>						
6	Rhodonite, tridymite, spessartite.	38	13	49	Eutectic	1140 ± 10
7	Rhodonite, spessartite, tephroite.	50	11	39	"	1160 ± 15
<i>Quintuple Points Established by Initial Cooling.</i>						
A	Spessartite, tridymite, "extinction crystals."	29	20	51	...	1120 ± 20
B	Tridymite, "extinction crystals," mullite.	27	22	51	...	1145 ± 10
C	Spessartite, "extinction crystals," mullite.	31	23	46	...	1145 ± 10
D	Spessartite, mullite, corundum.	33	24	43	...	1160 ± 10

very thin plates, embedded in glass. The crystals were optically negative and a few twins were commonly found. Accordingly it was suggested, but not conclusively proved, that the "extinction crystals" were MnO.Al₂O₃.2SiO₂, the

"extinction crystals" did not reappear until the mass was heated at a temperature high enough to destroy the crystals of 2MnO.2Al₂O₃.5SiO₂. Accordingly, a pseudo equilibrium diagram (see Fig. 3) was postulated to account for this portion of the system. The quintuple points are given in Table I.

As spessartite is isotropic, it can be identified only by its crystal form and by X-rays. Snow makes the interesting point that the metallographer will probably call this compound a "spinel." In specimens not suitable for X-ray examination it is almost impossible to differentiate between garnet and spinel, because, although on long treatment the garnet is decomposed by concentrated hydrofluoric acid and the spinel is not attacked, in polished sections any glass present in the inclusion is completely destroyed.

Present Investigation.

MnO was prepared from manganese oxalate by the method described by Hay and his co-workers.^{8,9} All the ternary melts were prepared from MnO, pure Al₂O₃, and silica sand (99.7% of SiO₂). The various melts were prepared in small platinum crucibles, heated in a small platinum-wound furnace in which the atmosphere could be controlled. The majority of the mixtures were heated in hydrogen, but a few were heated in nitrogen which had been passed over heated copper turnings to remove the small traces of oxygen. The furnace was so designed that melting could be observed through a low-power microscope.

Each mixture was melted and held at a temperature above its melting point for a short period to ensure completion of the reaction before heat-treatment was carried out. In some cases long annealing periods were required to facilitate

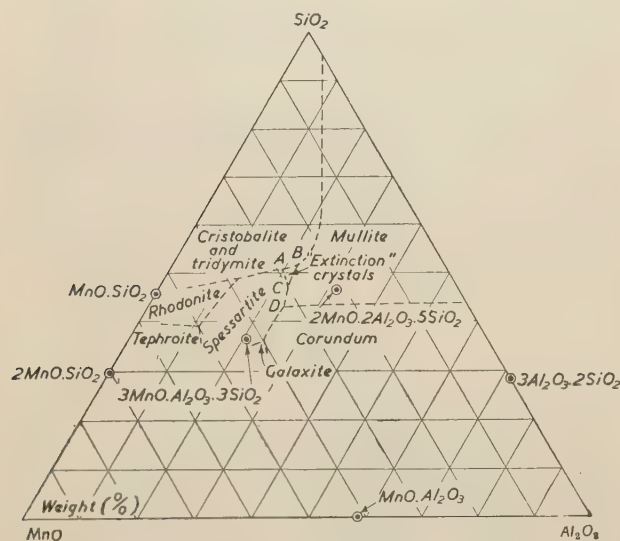


FIG. 3.—Pseudo Equilibrium Diagram obtained on cooling liquids consisting of MnO, SiO₂, and Al₂O₃ (according to Snow⁷).

manganese analogue of anorthite (CaO.Al₂O₃.2SiO₂). Confirmation was not obtained from the X-ray films, which were very disappointing. The behaviour of these two phases is very complex. The "extinction crystals" did not form above 1145° C., and on heating to 1155° C. they decomposed into mullite and liquid. After several heating and cooling cycles between 1120° and 1150° C., a crushed mass of "extinction crystals" transformed gradually to 2MnO.2Al₂O₃.5SiO₂;

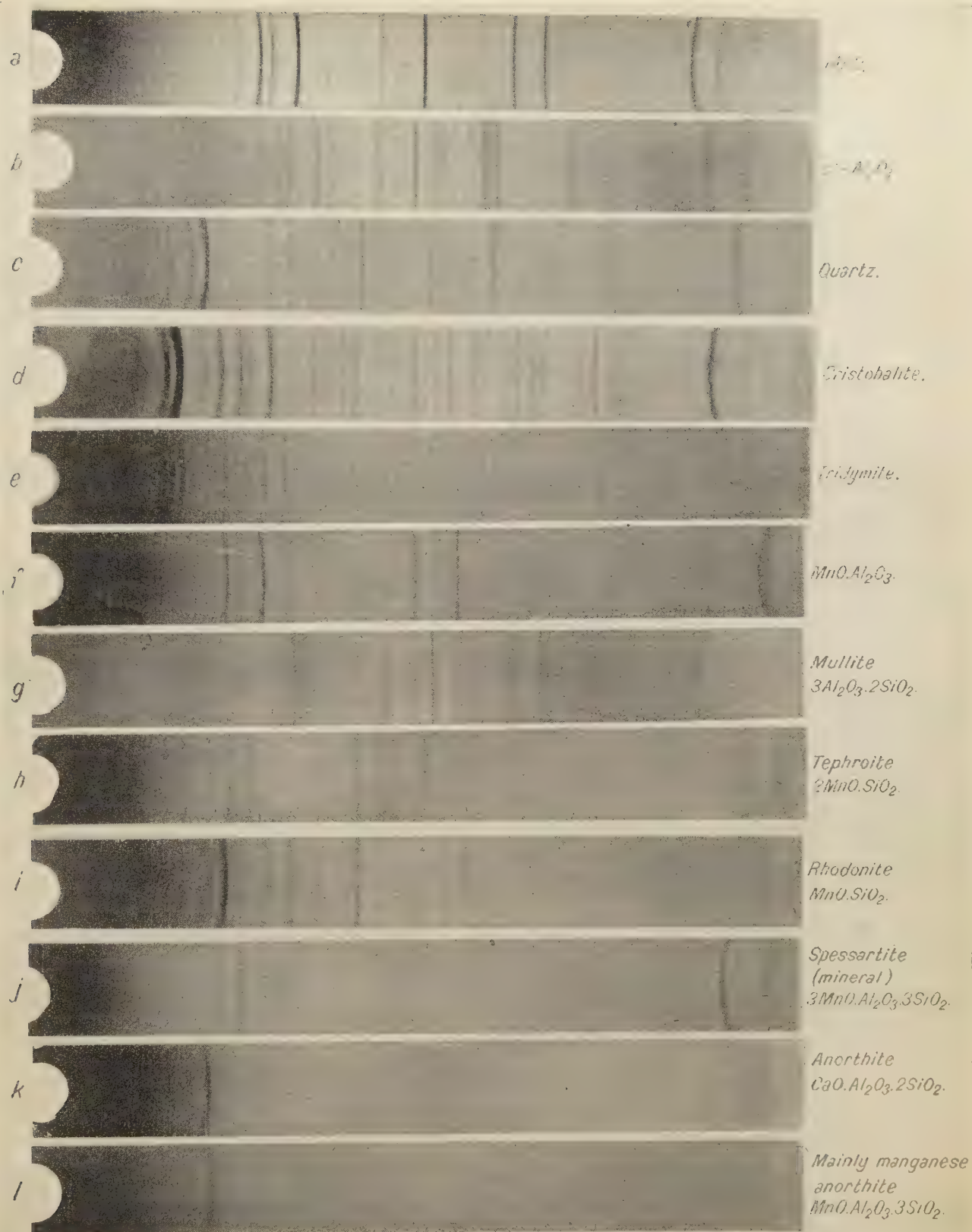


FIG. 4.—MnO—Al₂O₃—SiO₂ System : Typical X-Ray Photographs (Mn Radiation).

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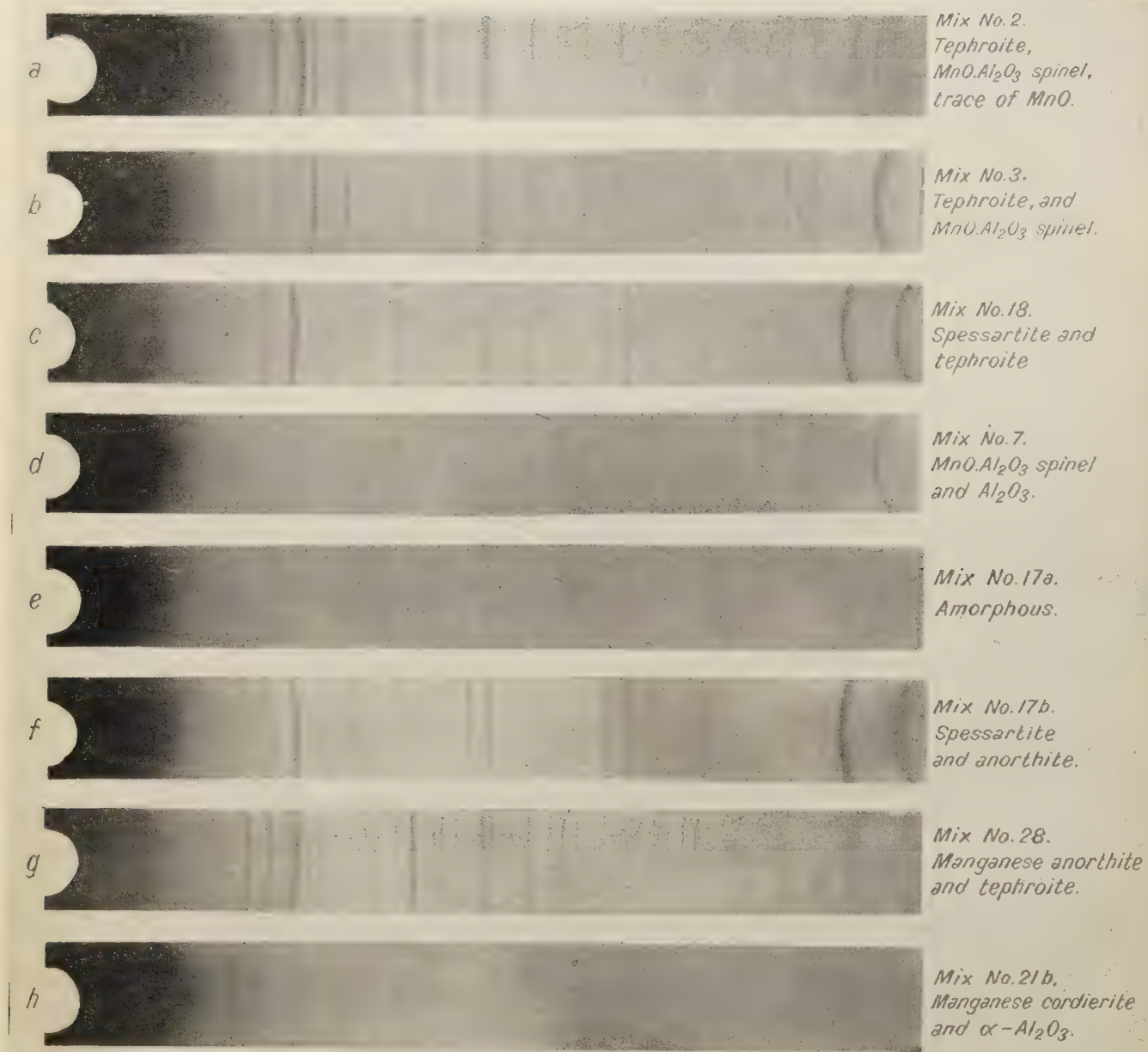


FIG. 5.—X-Ray Powder Photographs.



FIG. 6.—Mix No. 6. Tephroite and $\text{MnO} \cdot \text{Al}_2\text{O}_3$ spinel. Unetched. $\times 200$.

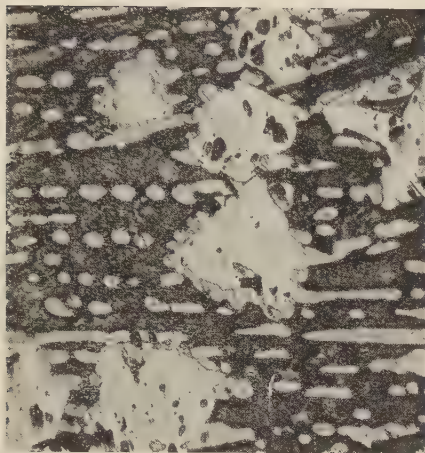


FIG. 7.—Mix No. 6. Tephroite and $\text{MnO} \cdot \text{Al}_2\text{O}_3$ spinel. Etched with alkaline sodium picrate. $\times 200$.

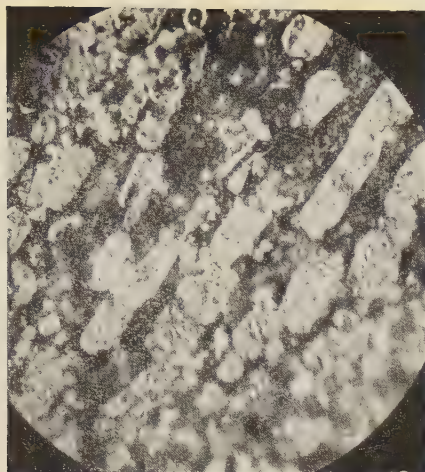


FIG. 8.—Mix No. 16. Spinel, tephroite and spessartite. Etched with alkaline sodium picrate. $\times 500$.

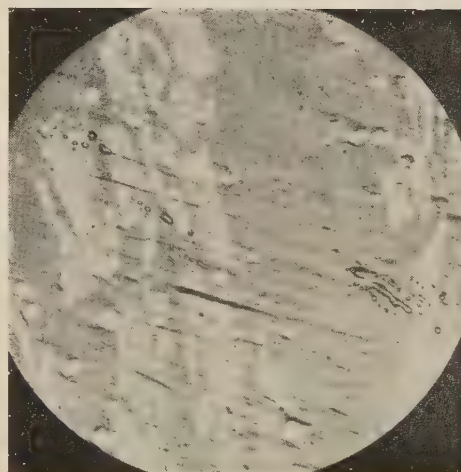


FIG. 9.—Mix No. 18. Tephroite and spessartite. Unetched. $\times 500$.

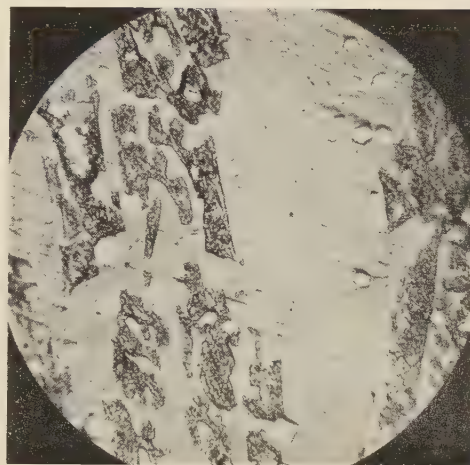


FIG. 10.—Mix No. 18. Tephroite and spessartite. Etched with dilute hydrochloric acid. $\times 500$.

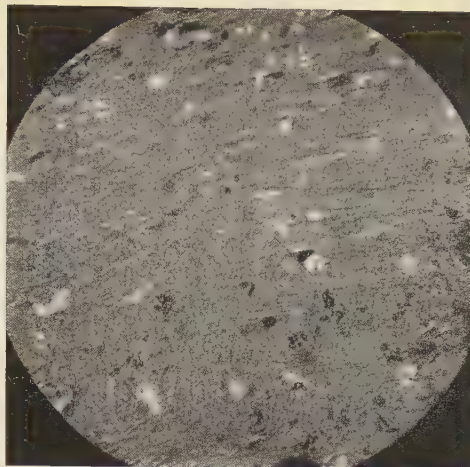


FIG. 11.—Mix No. 2. Tephroite, $\text{MnO} \cdot \text{Al}_2\text{O}_3$ spinel, and MnO . Unetched. $\times 500$.

(Micrographs reduced to four-fifths linear in reproduction.)

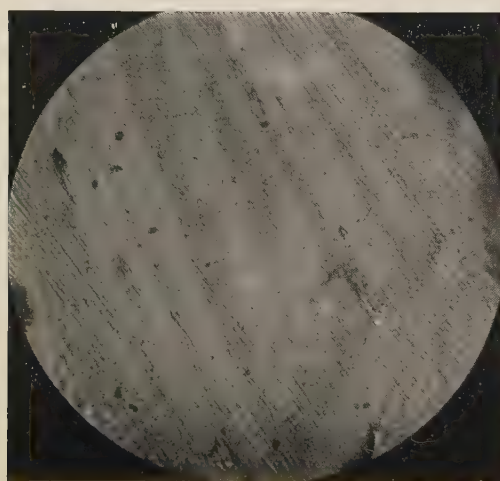


FIG. 12.—Mix No. 15. Rhodonite and some glass. Unetched. $\times 500$.



FIG. 13.—Mix No. 7. $\text{MnO} \cdot \text{Al}_2\text{O}_3$ spinel and Al_2O_3 . Unetched. $\times 500$.

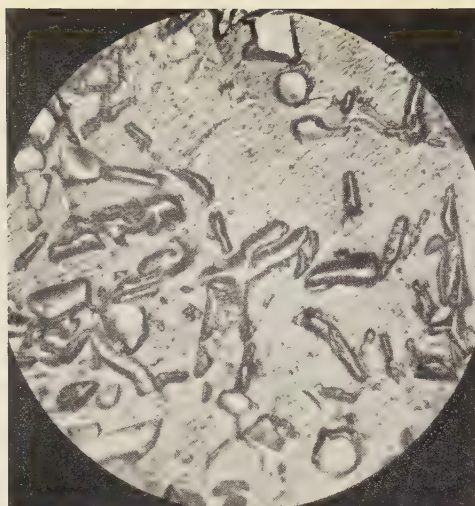


FIG. 14.—Mix No. 10. Al_2O_3 with trace of $\text{MnO} \cdot \text{Al}_2\text{O}_3$ spinel. Unetched. $\times 500$.



FIG. 15.—Mix No. 11. Chiefly Al_2O_3 . Unetched. $\times 500$.

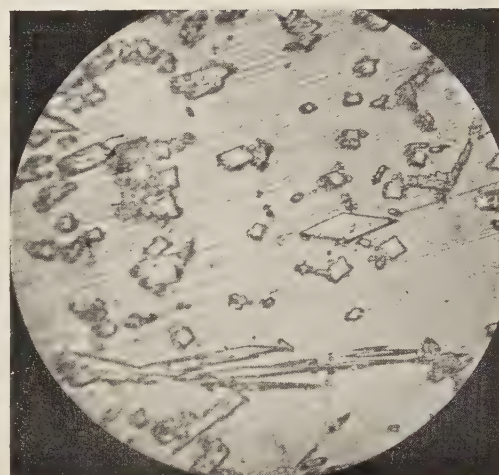


FIG. 16.—Mix No. 14. Mullite. Etched with alkaline sodium picrate. $\times 500$.

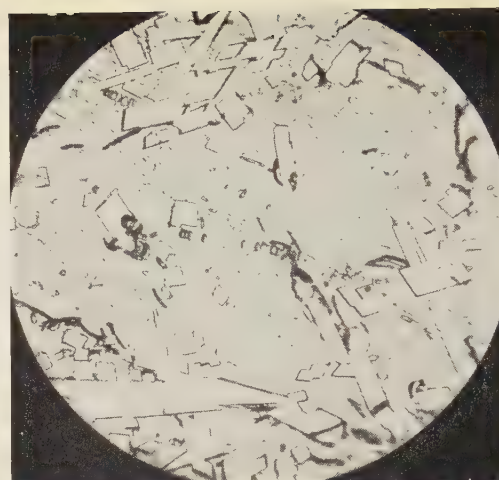


FIG. 17.—Mix No. 19. Anorthite with trace of spinel. Etched with alkaline sodium picrate. $\times 500$.

(Fig. 13 reduced to two-thirds, and remainder to four-fifths, linear in reproduction.)

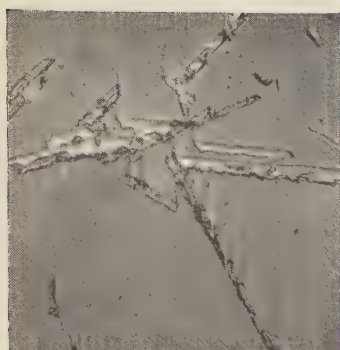


FIG. 18.—Mix No. 9. Al_2O_3 and glass. Unetched. $\times 500$.

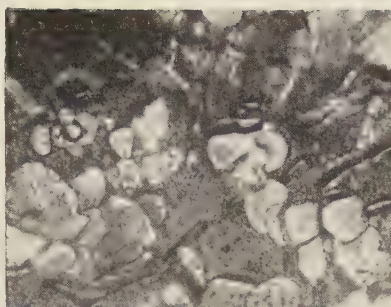


FIG. 19.—Mix No. 11. Al_2O_3 and twinned manganese anorthite. Etched with hydrofluoric acid. $\times 500$.

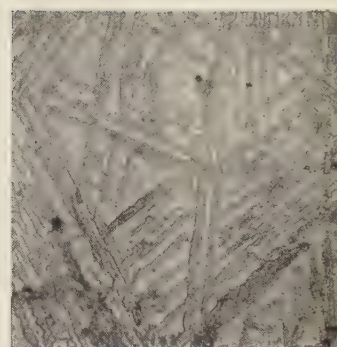


FIG. 20.—Mix No. 9. Spessartite and manganese anorthite. Etched with alkaline sodium picrate. $\times 500$.

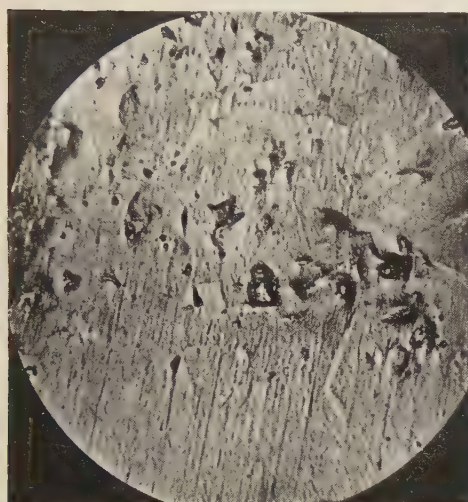


FIG. 21.—Mix No. 12. Mullite and Al_2O_3 . Unetched. $\times 500$.

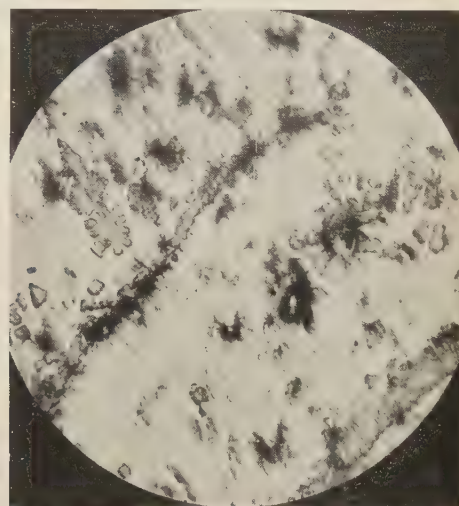


FIG. 22.—Mix No. 1. Cristobalite and glass. Etched with alkaline sodium picrate. $\times 500$.



FIG. 23.—Mix No. 13. Mullite and glass. Etched with alkaline sodium picrate. $\times 200$.

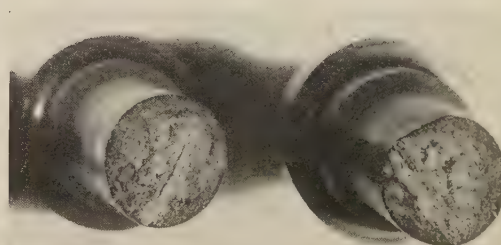


FIG. 24.—Striated Fractures in Tensile Test-Pieces. $\times 2$.

(Micrographs reduced to four-fifths linear in reproduction.)

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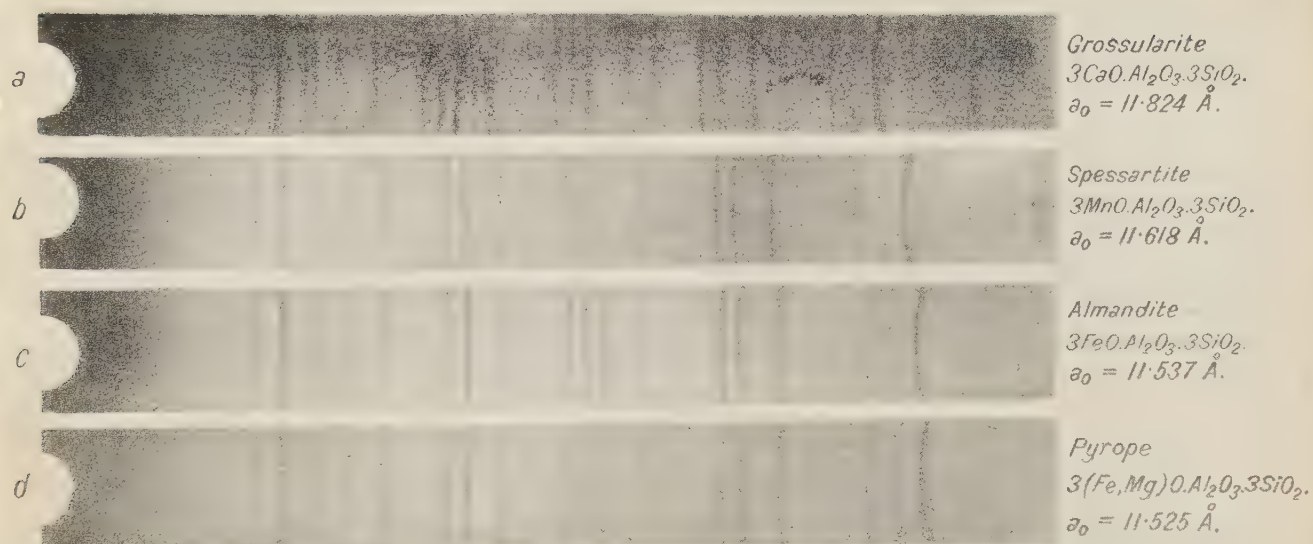


FIG. 25.—X-Ray Powder Photographs.



FIG. 26.—Typical Stringers of Manganese Aluminosilicate. Unetched. $\times 500$. (Reduced to four-fifths linear in reproduction.)

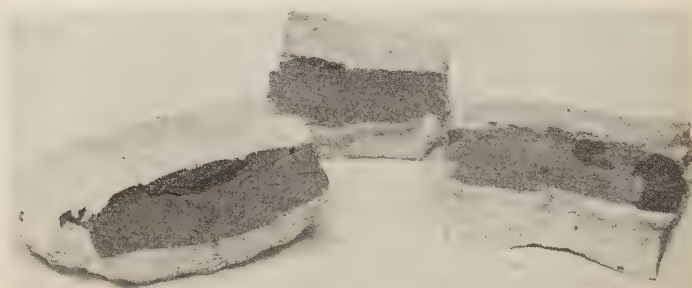


FIG. 27.—Aluminous Refractory.

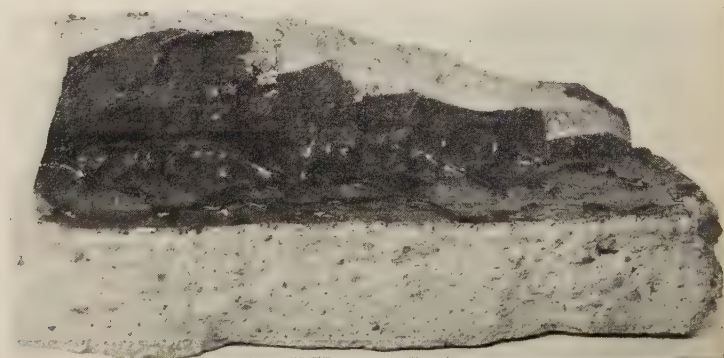


FIG. 28.—Ordinary Refractory, showing layer of manganese aluminosilicate slag.

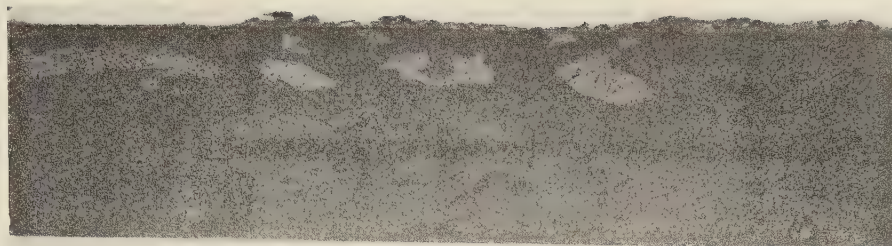


FIG. 29.—Steel Core from aluminous refractory.



FIG. 30.—Steel Core from ordinary refractory.

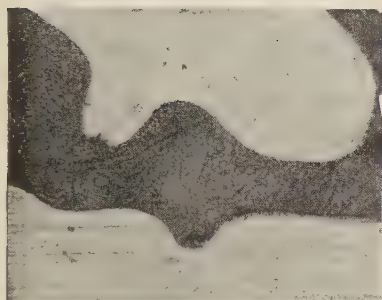


FIG. 31.—Ex.1. Manganese anorthite (large), mullite, and cristobalite (small). From runner scrap. $\times 500$.

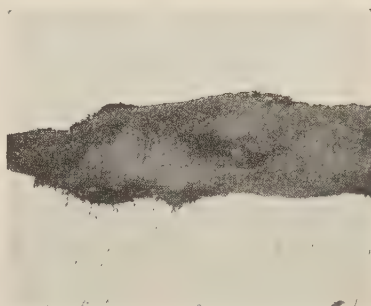


FIG. 32.—Ex.1. Similar inclusion to that shown in Fig. 31. From forging. $\times 500$.

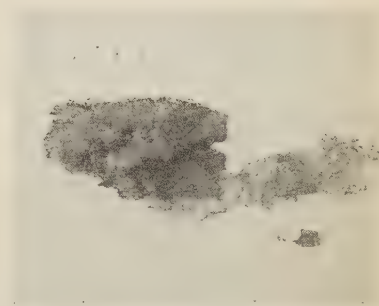


FIG. 33.—Ex.2. Spinel and spessartite. $\times 500$.

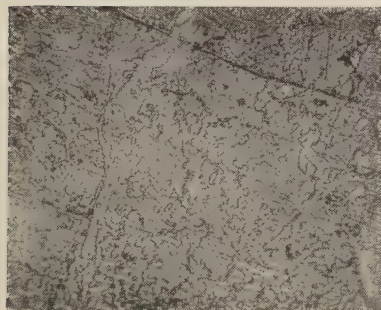


FIG. 34.—Ex.2. Spessartite and spinel. $\times 500$.

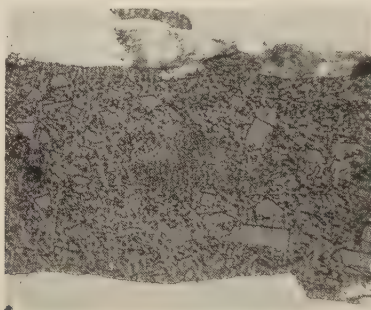


FIG. 35.—Ex.2. Slag from runner brick, showing mullite. Unetched. $\times 500$.

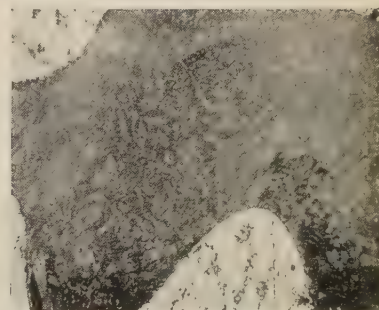


FIG. 36.—Ex.3. Spinel and pyroxene. $\times 500$.

Microspecimens etched with alkaline sodium picrate unless otherwise stated.
(Micrographs reduced to four-fifths linear in reproduction.)

[Rait and Pinder.

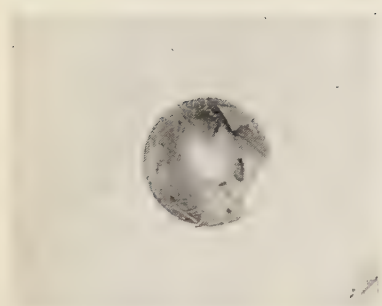


FIG. 37.—Ex.3. Spinel and needles of Al_2O_3 . Unetched. $\times 500$.

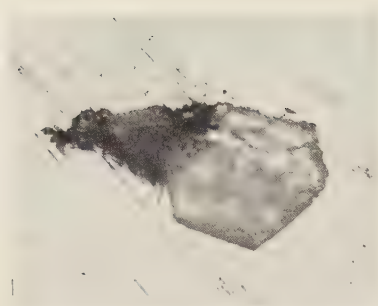


FIG. 38.—Ex.4. Aluminous inclusions. Unetched. $\times 500$.

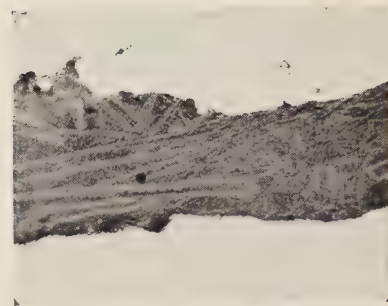


FIG. 39.—Ex.5. Rhodonite and pyroxene. $\times 500$.

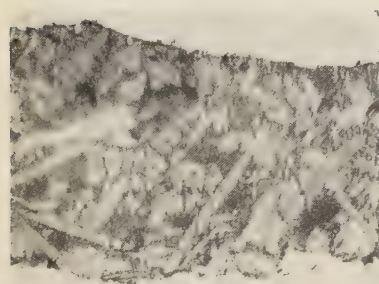


FIG. 40.—Ex.5. Manganese anorthite and pyroxene. $\times 500$.

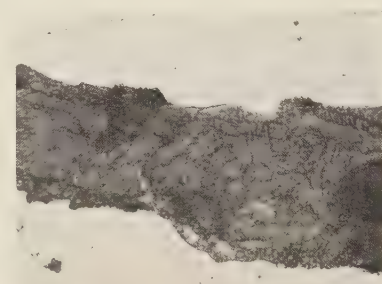


FIG. 41.—Ex.6. Manganese anorthite and pyroxene. $\times 500$.

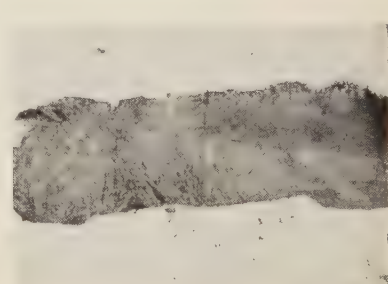


FIG. 42.—Ex.7. Complex structure. Rhodonite and manganese anorthite. $\times 500$.

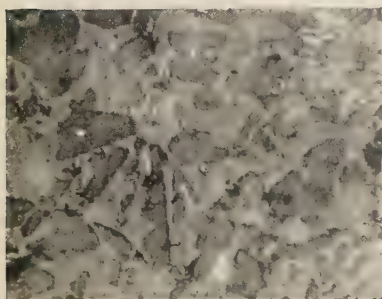


FIG. 43.—Ex.8. Free silica and pyroxene (from acid open-hearth slag). Unetched. $\times 500$.

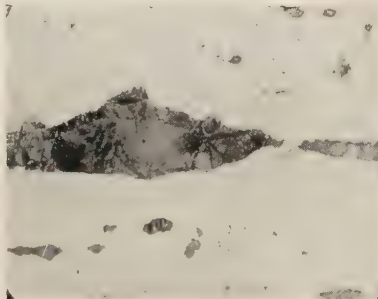


FIG. 44.—Ex.9. Silica and spinel. Unetched. $\times 500$.

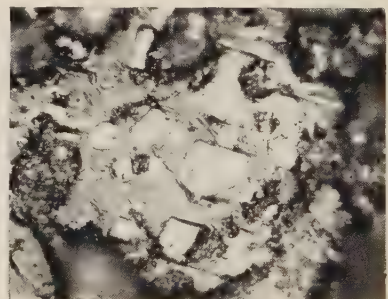


FIG. 45.—Ex.9. Spinel. Unetched. $\times 500$.

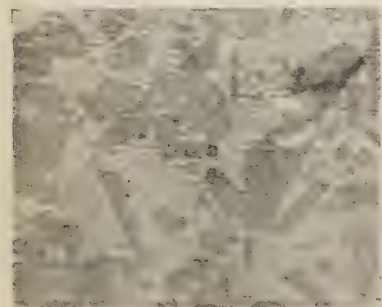


FIG. 46.—Ex.9. Free silica in silicate ground-mass. Unetched. $\times 500$.

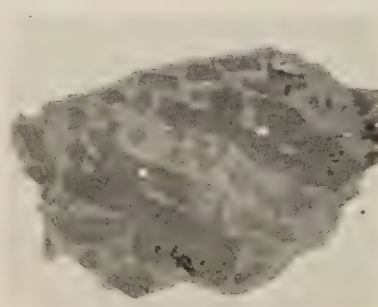


FIG. 47.—Ex.10. Inclusion similar to that shown in Fig. 46. Unetched. $\times 500$.

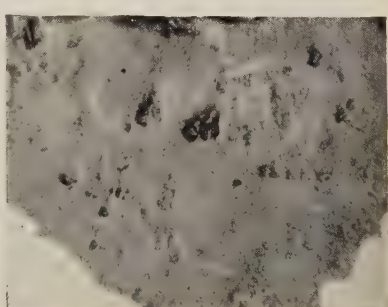


FIG. 48.—Ex.11. Free silica. Unetched. $\times 500$.

Specimens etched with alkaline sodium picrate unless otherwise stated.
(Micrographs reduced to four-fifths linear in reproduction.)

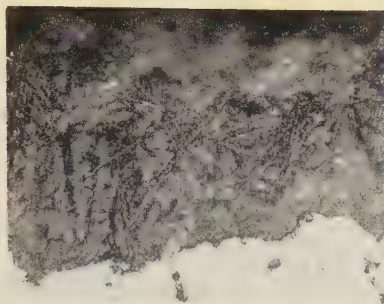


FIG. 49.—Ex.11. Rhodonite, manganese anorthite, and free silica. $\times 500$.



FIG. 50.—Ex.12. Free silica. Etched with hydrofluoric acid. $\times 500$.

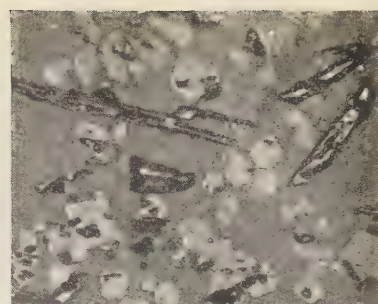


FIG. 51.—Ex.14. Spinel and Al_2O_3 laths. Unetched. $\times 500$.

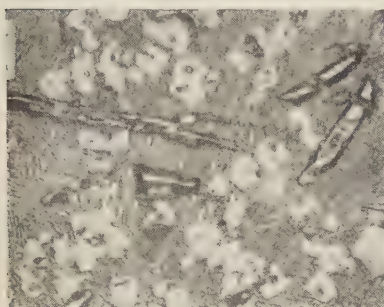


FIG. 52.—Ex.14. Same inclusion as in Fig. 51. Spinel, Al_2O_3 laths, and a eutectic. $\times 500$.

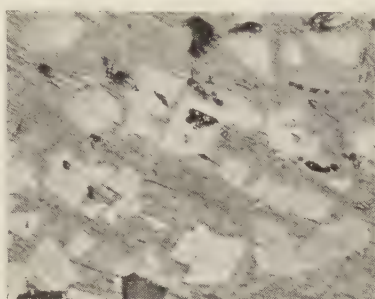


FIG. 53.—Ex.14. Spinel and pyroxene. Unetched. $\times 500$.

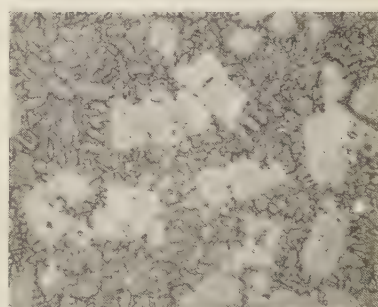


FIG. 54.—Ex.14. Same inclusion as Fig. 53. $\times 500$.



FIG. 55.—Ex.16. Rhodonite from tun-dish scum. $\times 500$.

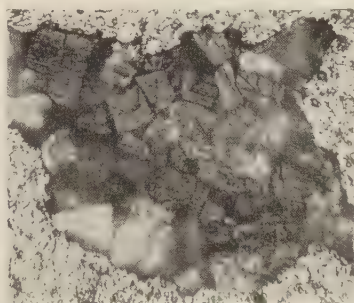


FIG. 56.—Ex.18. Gehlenite. $\times 500$.

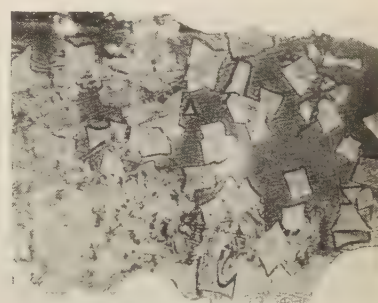


FIG. 57.—Ex.20. Gehlenite. $\times 500$.

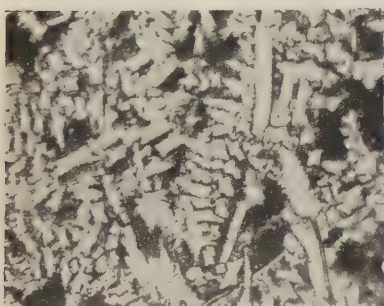


FIG. 58.—Ex.21. Gehlenite (in slag from firebrick portion of nozzle). $\times 500$.



FIG. 59.—Ex.26. Inclusions of silica. Unetched. $\times 500$.

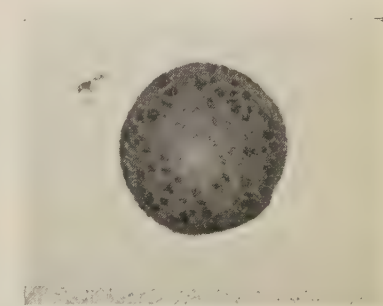


FIG. 60.—Ex.26. Silica in a silicate ground-mass. Unetched. $\times 500$.

Specimens etched with alkaline sodium picrate unless otherwise stated.
(Micrographs reduced to four-fifths linear in reproduction.)

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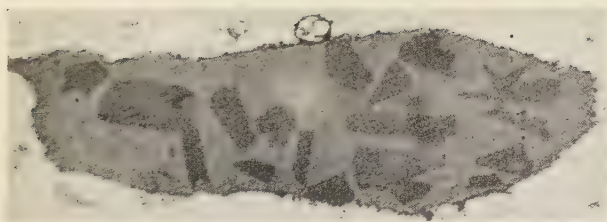


FIG. 61.—Ex.15. Free silica. Unetched. $\times 500$.

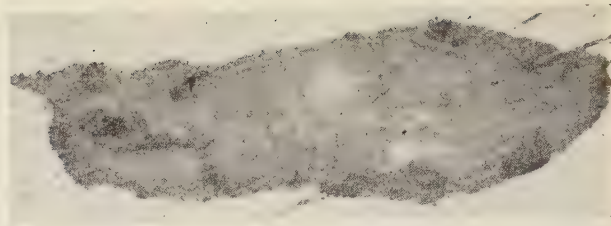


FIG. 62.—Ex.15. Same inclusion as in Fig. 61. Etched with hydrofluoric acid. $\times 500$.

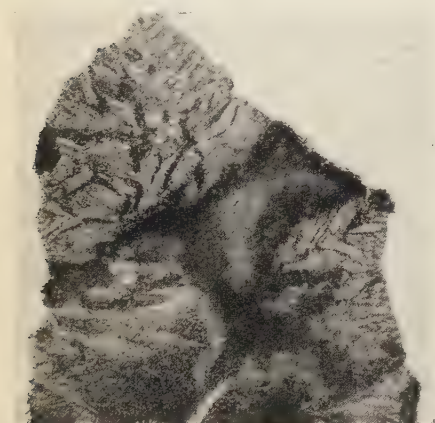


FIG. 63.—Ex.16. Rhodonite. Etched with alkaline sodium picrate. $\times 500$.

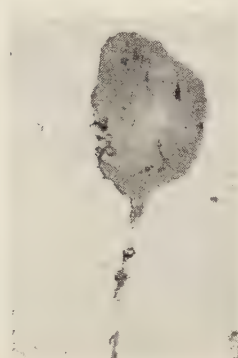


FIG. 64.—Ex.22. $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel and Al_2O_3 . Etched with alkaline sodium picrate. $\times 500$.

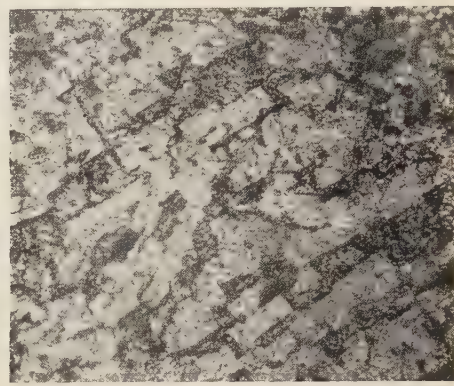


FIG. 65.—Ex.21. $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel (in slag from magnesite portion of nozzle). Etched with hydrofluoric acid. $\times 500$.



FIG. 66.—X-Ray Powder Photographs.

(Figs. 61, 62, and 65 reduced to four-fifths, and Fig. 63 to two-thirds, linear in reproduction.)

[Rait and Pinder.]

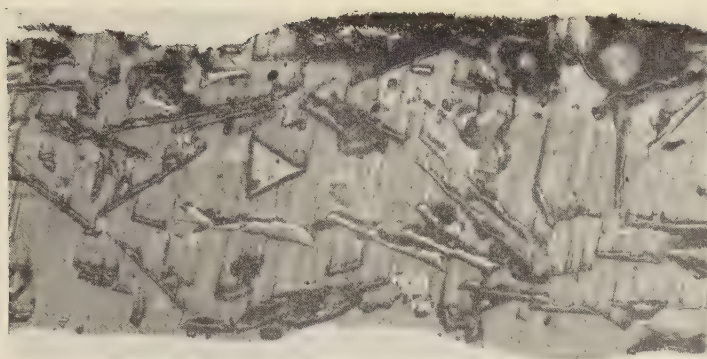


FIG. 67.—Ex.13. Laths and crystals of Al_2O_3 . Unetched. $\times 200$.

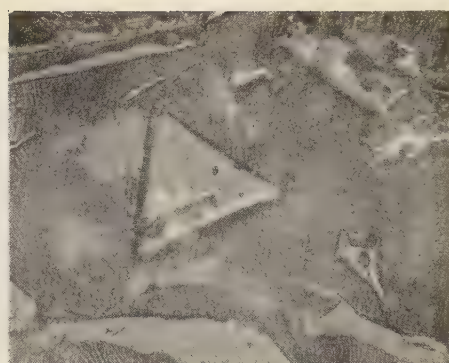


FIG. 68.—Ex.13. Same inclusion as in Fig. 67, showing Al_2O_3 and eutectic containing Al_2O_3 . $\times 500$.

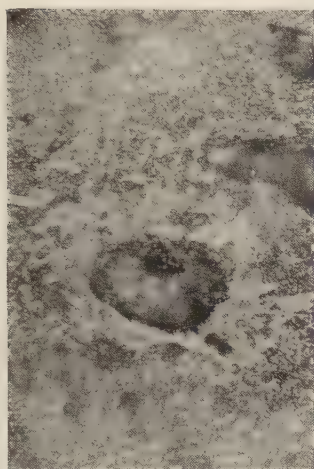


FIG. 69.—Ex.16. Mullite and cristobalite (from tundish scum). $\times 500$.



FIG. 70.—Ex.21. Spinel and gehlenite. $\times 500$.

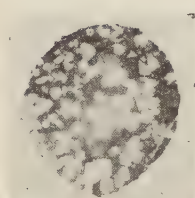


FIG. 71.—Ex.22. $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel. Unetched. $\times 500$.

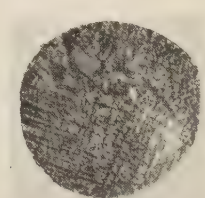


FIG. 72.—Ex.26. Inclusion showing appearance of rhodonite. $\times 500$.

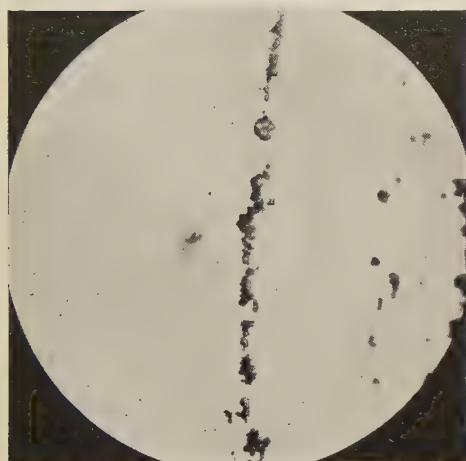


FIG. 73.—Ex.24. Stringer of alumina (see Fig. 85). Unetched. $\times 500$.

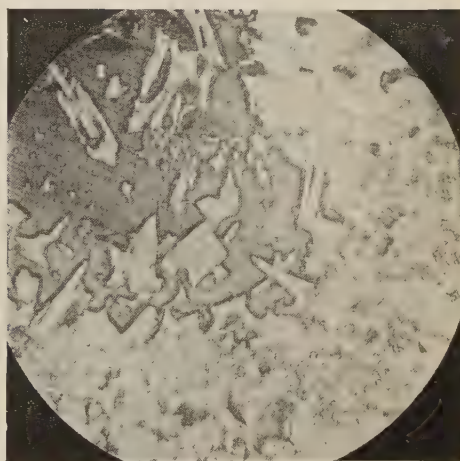


FIG. 74.—Ex.25. Diopside. $\times 500$.

Specimens etched with alkaline sodium picrate unless otherwise stated.
(Micrographs reduced to four-fifths linear in reproduction.)

[Rait and Pinder.]



FIG. 75.—Ex.23. Inclusion stringer. Unetched. × 500.

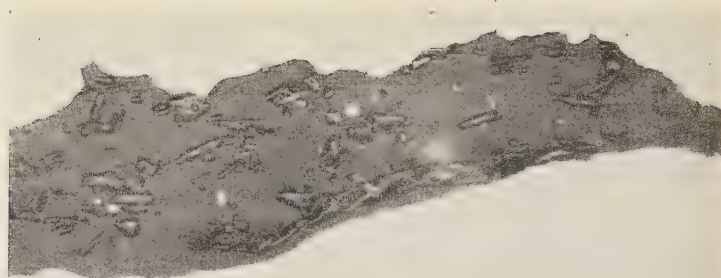


FIG. 76.—Ex.23. Inclusion as in Fig. 75, showing laths of Al_2O_3 . Unetched. × 500.

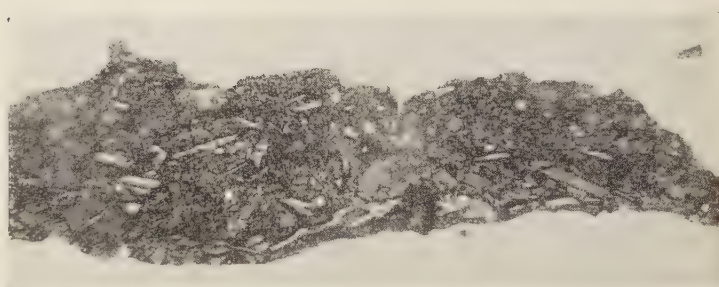


FIG. 77.—Ex.23. Inclusion as in Fig. 75, showing Al_2O_3 and mullite. × 500.

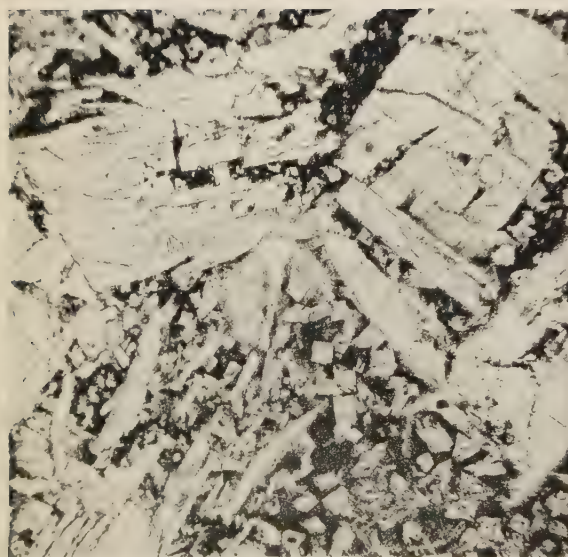


FIG. 78.—Slag layer from basic-electric ladle bricks, showing gehlenite.

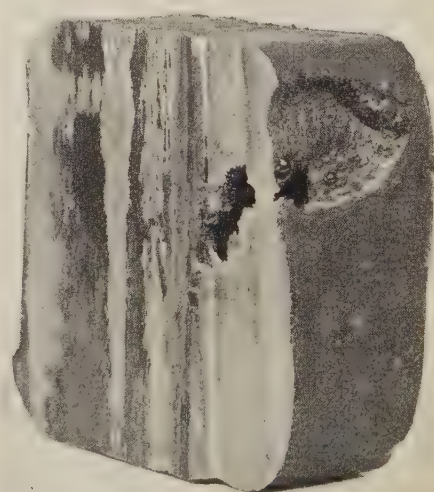


FIG. 79.—Section of metal runner, showing beads of aluminosilicate inclusions which enter the steel.

Micro-specimens etched with alkaline sodium picrate unless otherwise stated.
(Figs. 75 to 77 reduced to four-fifths, and Fig. 78 to two-thirds, linear in reproduction.)

[Rait and Pinder.]

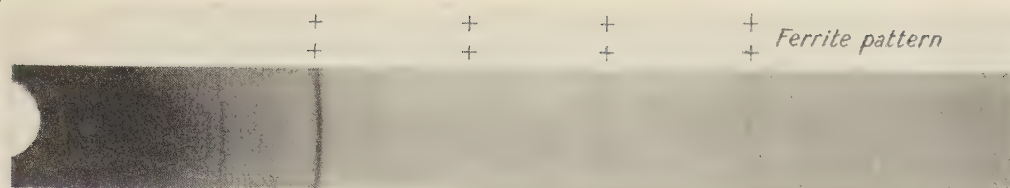


FIG. 80.—Ex.18. X-ray photograph showing gehlenite, pyroxene, and $3\text{CaO}.\text{SiO}_2$.

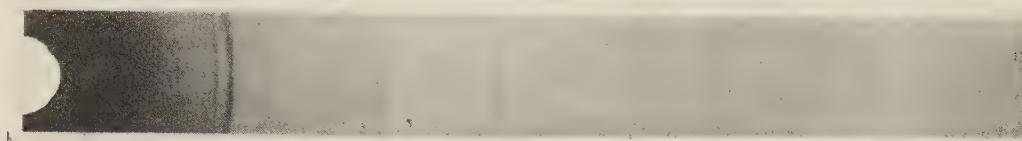


FIG. 81.—Ex.19. X-ray photograph showing gehlenite and anorthite.

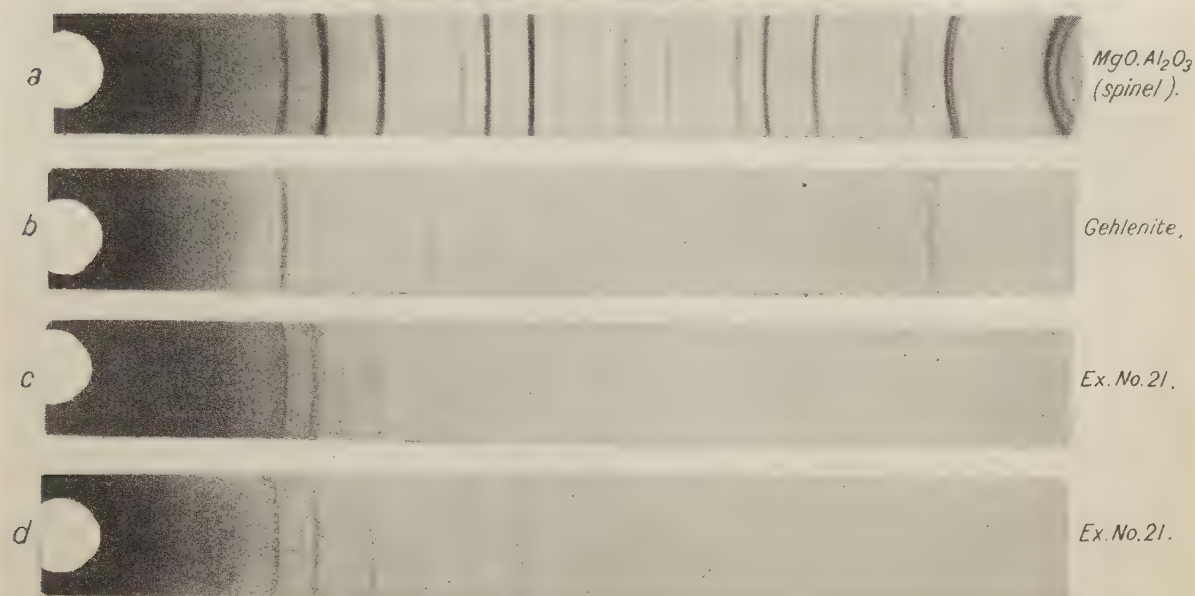


FIG. 82.—X-Ray Photographs.

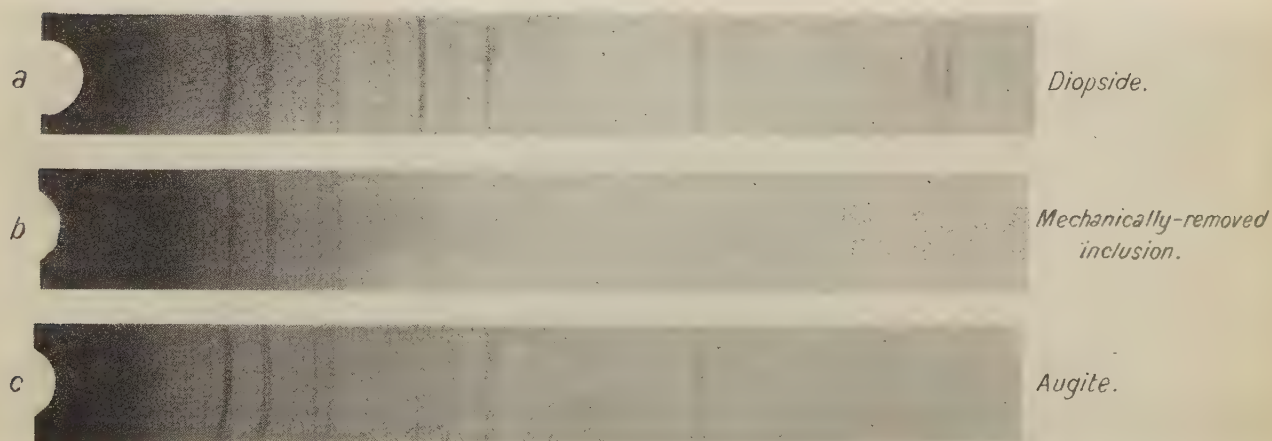


FIG. 83.—Ex.25. X-Ray Powder Photographs of Isomorphous Series.

[Rait and Pinder.



FIG. 84.—X-Ray Powder Photographs.

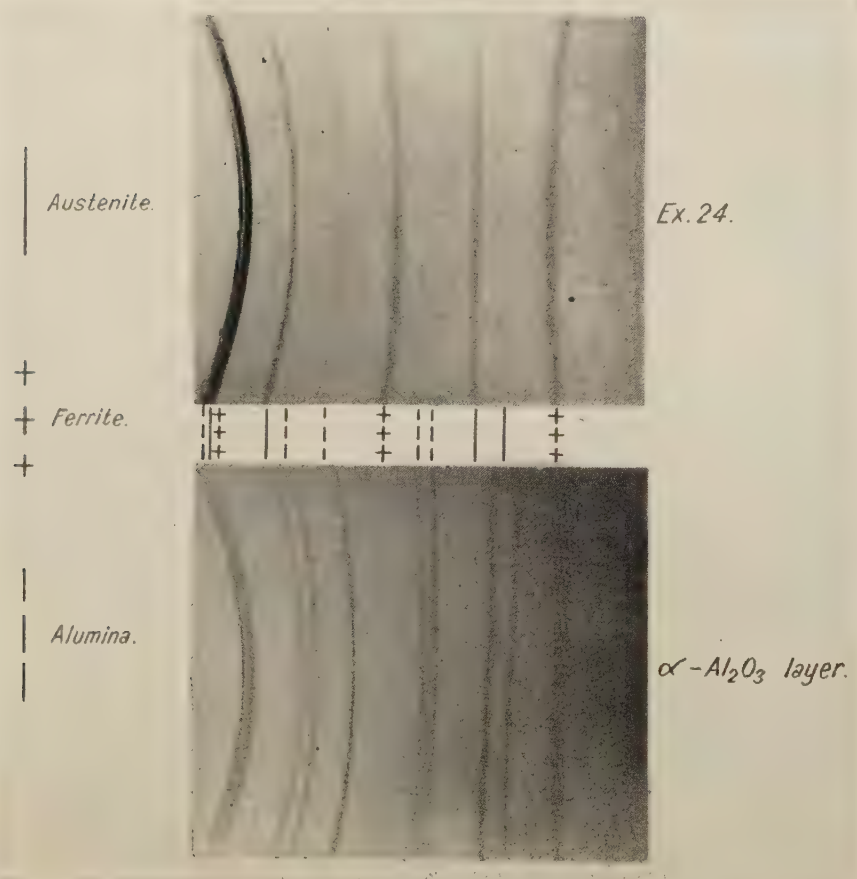


FIG. 85.—X-Ray Glancing-Angle Photographs.

crystallization. Each specimen was polished for microscopic examination by reflected light, and after the etched and unetched surfaces had been examined the specimen was crushed for examination by the X-ray powder method, manganese $K\alpha$ radiation being used throughout.

The details of the mixes and their thermal treatments are summarized in Table II, which also contains their constitutions as determined by the X-ray and microscopic methods. X-ray photographs of the various compounds and a few of the mixes are reproduced in Figs. 4 and 5, and some typical photomicrographs are reproduced in Figs. 6 to 23.

Discussion of the Results.

Three ternary compounds have been identified in this system, namely, manganese feldspar, spessartite garnet, and the manganese analogue of cordierite.

Manganese Feldspar.

A compound with the typical plagioclase-feldspar X-ray pattern occurs in a number of the ternary mixtures. The plagioclase feldspars are triclinic, the isomorphous series extending from albite ($\text{Na}.\text{Al}_2\text{Si}_3\text{O}_8$) to anorthite ($\text{Ca}.\text{Al}_2\text{Si}_2\text{O}_8$). The lattice is based on chains of SiO_4 tetrahedral groups in which Si^{++++} (and Al^{+++}) ions are surrounded by four O^{--} ions. Four tetrahedra are linked to form rings, in which the vertices alternately point in opposite directions, the rings being placed over each other to join in a chain. The chains run parallel to the a axis, the main cleavages being parallel to them. The silicon at the centre of the tetrahedron can be substituted by aluminium to varying degrees. For instance, a quarter of the Si^{++++} ions are replaced in albite and a half in anorthite. The alkali and alkaline-earth ions (K^+ , Na^+ , Ba^{++} , Ca^{++}) fill the cavities within the framework of tetrahedra. Reference should be made to papers by Taylor,¹⁷ Schiebold,¹⁸ and Bragg,¹⁹ for more detailed information. The existence of a manganese feldspar is a new feature, and contrasts with the following quotation from Bragg: "In all the feldspar structures, the only places for cations apart from the silicon-aluminium-oxygen framework are the large cavities described above. It is therefore not surprising to find that the feldspars contain only large ions such as Na, K, Ca, and Ba. They do not, for instance, contain the series of small ions Mg, Fe, Cr, Mn, &c., which enter so freely into the structures of pyroxenes, amphiboles, and the mica minerals. The structure has no suitable place for ions which require a situation within an octahedral group." However, the X-ray pattern shows that the compound is a true feldspar and since it crystallizes in greatest amount from mixtures close to the composition $\text{MnO}.\text{Al}_2\text{O}_3.2\text{SiO}_2$, it would appear to be a true

manganese analogue of anorthite, as suggested by Snow.⁷

The optical properties were similar to those reported by Snow, twinning being a notable feature. Typical primary crystals of manganese anorthite are shown in Fig. 17.

Spessartite Garnet.

The occurrence of a primary field of spessartite garnet in the centre of the system has been confirmed. These crystals are isotropic, with a high refractive index (1.8^+); the crystals are usually six-sided, the smaller crystals appearing rounded. The crystals appeared light grey in colour when etched with alkaline sodium picrate. X-ray powder photographs show that this phase has the same structure as natural garnet (see Fig. 25(b)), the spacing being $a_0 = 11.618 \text{ \AA}$. According to Snow, spessartite is the only member of the garnet family to have a stability range on the liquidus surface. However, a number of mixtures lying in the primary spessartite field, which had been quenched from much higher temperatures than the melting point of spessartite (1200°C .) and subsequently annealed at 900°C ., did not contain spessartite, but manganese anorthite and tephroite. It would therefore appear that spessartite dissociates above 1200°C . to form manganese anorthite and liquid which quenches to a glass; tephroite crystallizes from this glass on subsequent annealing at 900°C . As illustrated in the micrographs, it is impossible to distinguish between spessartite and spinel by reflected light, since the crystal form and the action of etching reagents are almost identical in the two cases; the only satisfactory method is by the use of X-rays. Since this latter method can rarely be applied to inclusions *in situ* in steel, it is difficult to differentiate between these compounds in non-metallic inclusions.

The Manganese Analogue of Cordierite.

A compound with a similar X-ray pattern to that of cordierite ($2\text{MgO}.2\text{Al}_2\text{O}_3.5\text{SiO}_2$), but with a considerably larger spacing (as is to be expected with the replacement of Mg^{++} by Mn^{++}), was found in one mixture. The rare occurrence of this compound confirms Snow's findings that it crystallizes only from melts on initial cooling and then with great difficulty.

The coexisting phases in the annealed mixes are illustrated in Fig. 86, and are summarized as follows:

- (1) Manganous oxide, tephroite, galaxite.
- (2) Tephroite, spessartite, galaxite.
- (3) Tephroite, rhodonite, spessartite.
- (4) Spessartite, galaxite, corundum.
- (5) Spessartite, manganese feldspar, corundum.
- (6) Manganese feldspar, corundum, mullite.
- (7) Manganese feldspar, mullite, cristobalite or tridymite.

TABLE II.—*Details of Constitution, Appearance, Heat-Treatment, and Examinations of the Mixes.*

Mix No.	Composition, wt.-%.			Heat-Treatment.	Appearance of Melt.	Micro-Examination.	X-Ray Examination.
	MnO.	Al ₂ O ₃ .	SiO ₂ .				
1	27	18	55	Heated to 1500° C., held at 1400° C. for 3 hr., and quenched. Annealed 3 hr. at 1300° C., then quenched.	Yellowish-pink glass. Partially crystalline.	Glassy. Medium-grey glass with trace of cristobalite. Cristobalite was readily attacked by alkaline sodium picrate solution; glass not attacked. (Fig. 22.)	Amorphous. Trace cristobalite and glass.
2(a)	70	10	20	Heated to 1390° C. (melt very fluid), held at 1150° C. for 3 hr., and quenched.	Brown.	Few rounded crystals of MnO, light grey in colour, in background of tephroite and spinel. (Fig. 11.)	Tephroite (large). MnO.Al ₂ O ₃ (medium). MnO (trace).
2(b)	70	10	20	Heated to 1380° C., held at 900° C. for 3 hr., and cooled during 3 hr.	Brown.	Few rounded crystals of MnO, light grey in colour, in background of tephroite and spinel. (Fig. 11.)	Tephroite (large). MnO.Al ₂ O ₃ (medium). MnO (trace).
3	70	20	10	Heated to 1400° C. and cooled slowly over period of 3 hr.	Brown.	Typical spinel crystals, and rather less of a medium-light grey phase of typical appearance of tephroite.	MnO.Al ₂ O ₃ (medium/large). Tephroite (medium/large).
4(a)	50	20	30	Heated to 1520° C. and quenched.	Medium greyish-brown colour.	No micro-section taken.	Mainly amorphous. MnO.Al ₂ O ₃ (small).
4(b)	50	20	30	Heated to 1450° C., cooled rapidly; heated to 900° C., held for 3 hr., and cooled during 3 hr.	Grey.	Mainly tephroite and glass. Small amount of spinel.	Tephroite (large). MnO.Al ₂ O ₃ (trace).
5	45	25	30	Heated to 1500° C. and cooled rapidly; annealed 100 hr. at 900° C.	Greyish-brown.	No micro-section taken.	Tephroite (large). MnO.Al ₂ O ₃ (medium).
6	52.6	20.0	27.4	Heated to 1300° C., held at 1050° C. for 3 hr., and quenched.	Medium dark greyish-brown colour. Opaque, probably cristobalite.	Mainly spinel crystals (medium grey with a violet tinge and more lustre than other phases); also medium light-grey phase, often of dendritic appearance, in some fields, showing characteristic appearance of tephroite. Also medium dark grey glass. In some fields the tephroite appeared to have been crystallized around the spinel. (Figs. 6 and 7.)	Tephroite (large). Spinel (medium).
7	35.0	45.0	20.0	Heated to 1470° C., held at 1300° C. for 3 hr., and quenched.	Opaque, greyish-brown.	Spinel crystals and laths of free alumina (about equal amounts) in a medium-grey glass. Glass attacked by alkaline sodium picrate. (Fig. 13.)	Spinel (large). Alumina (large).
8	40	30	30	Heated to 1550° C. and quenched.	Light greyish-brown.	...	Mainly amorphous. Alumina (small).
9	31.5	31.5	37	Heated to 1450° C., held at 1300° C. for 3 hr., and quenched. Same melt. Heated to 1100° C., held for 3 hr., and quenched.	Grey-yellow, largely glassy. Very light yellowish-grey colour.	Very fine needles of alumina in a medium-grey glass. (Fig. 18.) Some alumina needles still present, but main phases were a medium light-grey phase and a darker phase forming a criss-cross pattern similar to a Widmannstätten structure. Lighter phase believed to be spessartite, and darker phase anorthite. (Fig. 20.)	Largely glassy. Alumina (small). Spessartite (large). Anorthite (medium/large). Al ₂ O ₃ (trace).
10	26	46	28	Heated to 1500° C., held at 1150° C. for 3 hr., and quenched.	Yellowish-grey crystalline mass.	Alumina crystals in a medium-grey glass. Glass attacked by alkaline sodium picrate. (Fig. 14.)	Largely glassy. Al ₂ O ₃ (medium).
11	26	37	37	Heated to 1400° C., held at 1200° C. for 3 hr., and quenched.	Grey, opaque, shiny.	Two crystalline phases observed. Fine needles Al ₂ O ₃ . Few crystals, apparently of monoclinic or triclinic form and showing twinning. (Figs. 15 and 19.)	Largely glassy. Al ₂ O ₃ (medium). Probably trace of anorthite.
12	17.0	50.0	33.0	Heated to 1550° C., held at 1350° C. for 3 hr., and quenched.	Pinkish colour; porous; had not been completely molten.	Mullite and alumina, of about equal amounts. (Fig. 21.)	Mullite (large, and of normal pattern). Al ₂ O ₃ (large).
13	22.6	27.4	50	Heated to 1540° C., held at 1300° C. for 3 hr., and quenched.	Grey-yellow colour, partly glassy.	Medium-grey glass with crystals of rectangular and diamond-shaped section. Crystals only slightly lighter in colour than the glass and not readily seen in unetched condition. Alkaline sodium picrate showed up the outline of the crystals. Crystals apparently unattacked by dilute HF, but crystals outlined in depth, probably due to attack on glass at boundaries. (Fig. 23.)	Mostly glass. Mullite (small). (Lines of different relative intensities from those of normal mullite.)

[Continued overleaf.]

TABLE II.—(Continued).

Mix No.	Composition, wt.-%.			Heat-Treatment.	Appearance of Melt.	Micro-Examination.	X-Ray Examination.
	MnO.	Al ₂ O ₃ .	SiO ₂ .				
14	16.0	38.0	46.0	Heated to 1540° C.; quenched from 1350° C.	Medium-grey, rather porous. Had evidently not been completely molten.	Medium-grey glass with numerous crystals of mullite. (Fig. 16.)	Mullite, but lines of different relative intensities from those of standard mullite and mullite in mix No. 13.
15	47	8	45	Heated to 1300° C., held at 1150° C. for 3 hr., and quenched.	Pinkish-grey.	Large laths of rhodonite. Medium light-grey colour in a darker grey glass. (Fig. 12.)	Rhodonite (large). Spessartite (trace). Some glass.
16	43.2	20.8	36.0	Heated to 1230° C., held at 1150° C. for 3 hr., and quenched. Heated at 1195° C. for 4 hr. and quenched.	Opaque, showing greyish-brown; rather porous; had probably not been completely molten. Greyish-brown.	Some tephroite present, together with large amount of crystalline phase, often of appearance of spinel. Also more rounded crystals, of same colour as spinel. Medium-grey glass. (Fig. 8.) ...	Spinel (large). Spessartite (medium). Tephroite (small). Spessartite (medium). Spinel (medium).
17	30	20	50	Heated at 1550° C. and quenched. Heated to 1190° C., held for 3 hr., and cooled during 3 hr.	Light yellowish-grey. Light yellowish-grey.	Amorphous. Partly amorphous. Spessartite (large). Anorthite (medium).
18	40	20	40	Heated to 1150° C., held at 900° C. for 3 hr., and cooled during 3 hr.	Light pinkish in colour.	Tephroite crystals, together with crystals of hexagonal section, light grey in colour and much lighter after etching in dilute HCl. Believed to be spessartite. (Figs. 9 and 10.)	Spessartite (large). Tephroite (medium).
19	24.3	34.8	40.9	Heated to 1500° C., held at 1350° C. for 3 hr., and quenched.	Grey.	Triclinic crystals showing frequent twinning, in a medium-grey glass. (Fig. 17.)	Largely glassy. Anorthite (medium). Spinel (trace).
20	25	25	50	Heated to 1500° C. and quenched; annealed 100 hr. at 900° C.	Grey.	...	Anorthite only.
21(a)	30	30	40	Heated to 1600° C. and quenched.	Grey glass.	Glassy.	Mainly glass. Al ₂ O ₃ (trace).
21(b)	30	30	40	Annealed 100 hr. at 900° C.	Pale pinkish-buff colour.	No micro-examination.	α-Al ₂ O ₃ (small). Manganese. Cordierite (large).
21(c)	30	30	40	Heated to 1170° C.; annealed 3 hr. at 900° C.	Pink.	No micro-examination.	α-Al ₂ O ₃ (large). Manganese. Anorthite (medium).
22	55	10	35	Heated to 1550° C. and quenched.	Deep orange-pink glass.	Glassy.	Glassy.
23	50	15	35	Heated to 1550° C. and quenched. Annealed 100 hr. at 900° C.	Orange-pink glass. Greyish-brown.	Glassy. No micro-examination.	Glassy. Tephroite (large). MnO, Al ₂ O ₃ (small).
24	35	20	45	Heated to 1540° C. and quenched. Annealed 100 hr. at 900° C.	Amber glass. Greyish-yellow.	Glassy. No micro-examination.	Glassy. Tephroite (large). Manganese anorthite (large).
25	35	25	40	Heated to 1500° C. and quenched; annealed 100 hr. at 900° C.	Greyish-yellow.	No micro-examination.	Manganese anorthite (large). Al ₂ O ₃ (trace).
26	30	25	45	Heated to 1500° C. and quenched.	Pink glass.	Glassy.	Glassy.
27	40	15	45	Heated to 1650° C. and quenched. Annealed 100 hr. at 900° C.	Orange glass. Greyish-yellow.	Glassy. No micro-examination.	Glassy. Manganese anorthite (large). Tephroite (trace).
28	45	15	40	Heated to 1500° C. and quenched; annealed 100 hr. at 900° C.	Grey.	No micro-examination.	Manganese anorthite (medium/large). Tephroite (medium/large).
29	35	15	50	Heated to 1510° C. and quenched; annealed 100 hr. at 900° C.	Greyish-yellow.	No micro-examination.	Manganese anorthite (large). Tephroite (trace).
30	25	20	55	Heated to 1510° C. and quenched; annealed 100 hr. at 900° C.	Greyish-yellow.	No micro-examination.	Manganese anorthite (large). Tephroite (small).
31	45	20	35	Heated to 1510° C. and quenched; annealed 100 hr. at 900° C.	Greyish-yellow.	No micro-examination.	Tephroite (large). Manganese anorthite (small).

(8) Spessartite, manganese feldspar, cristobalite or tridymite.

(9) Spessartite, rhodonite, cristobalite or tridymite.

These coexisting phase-groups agree with Snow's pseudoequilibrium diagram (Fig. 3), with the exception of groups 5 and 6. Snow expressed some uncertainty about the phase grouping in this part of the system, but after considering the two alternatives (a) spessartite, anorthite, and mullite; spessartite, mullite, and

steel with firebrick material, since, as will be shown in later sections, the compositions of a large number of the slags formed by this reaction fall close to or within this area.

Snow's observation that some of the $\text{MnO-Al}_2\text{O}_3\text{-SiO}_2$ melts are very fluid, particularly those high in manganese, was confirmed.

THE SYSTEM $\text{FeO-MnO-SiO}_2\text{-Al}_2\text{O}_3$.

A detailed knowledge of the quaternary system $\text{FeO-MnO-SiO}_2\text{-Al}_2\text{O}_3$ would be of great value in the study of the constitution of non-metallic inclusions in steel. Although the system has not been investigated, certain deductions regarding phases likely to be encountered may be made from the available data on the bounding ternary systems, namely $\text{FeO-SiO}_2\text{-Al}_2\text{O}_3$,^{20, 21, 22} FeO-MnO-SiO_2 ,¹ $\text{FeO-MnO-Al}_2\text{O}_3$,²⁵ and $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3$.

The following phases will occur :

- (1) FeO with MnO in solid solution.
- (2) MnO with FeO in solid solution.
- (3) Tephroite-fayalite solid solutions ($(\text{Fe,Mn})\text{O} \cdot \text{SiO}_2$).

There is complete solid solution extending from fayalite to tephroite; the mineral knebelite, containing approximately equimolecular amounts of the two silicates, being a member of this series.

- (4) Spinel solid solutions ($(\text{Fe,Mn})\text{O} \cdot \text{Al}_2\text{O}_3$).

- (5) Rhodonite ($\text{MnO} \cdot \text{SiO}_2$) with partial solid solution extending towards the composition " $\text{FeO} \cdot \text{SiO}_2$."

Sundius²³ has reported the occurrence of pure iron rhodonite, isomorphous with rhodonite, while Whiteley and Hallimond²⁴ found rhodonite in low-lime acid slags when the ratio of MnO to FeO exceeded 27 : 73 approximately. White¹ considers that two distinct series may occur, though how they are related—whether as enantiotropes or otherwise—cannot be decided until a more detailed investigation of the system FeO-MnO-SiO_2 , particularly with regard to possible inversions in the solid state, is carried out.

- (6) Spessartite-garnet solid solution, extending towards $3\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$.

Although the iron-garnet almandite is found in nature, it does not appear in the ternary system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$. It is very probable that in the quaternary system $\text{FeO-MnO-SiO}_2\text{-Al}_2\text{O}_3$, partial replacement of the Mn by Fe in the spessartite garnet will occur.

- (7) Manganese anorthite ($\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$).

As the Fe^{++} ion is too small to occupy the cation position in the feldspar lattice, the ion anorthite does not exist and it is unlikely that even partial replacement of the Mn^{++} by Fe^{++} can occur in the manganese anorthite.

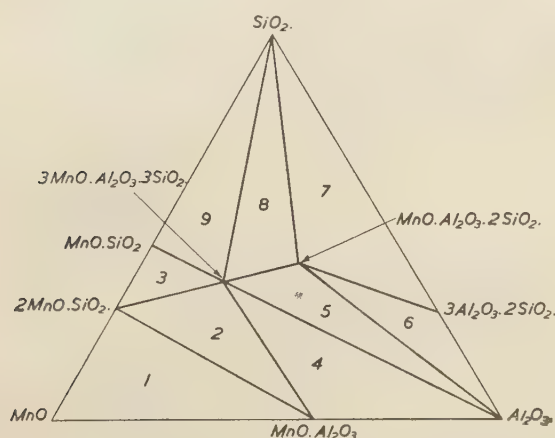


FIG. 86.—Ternary Diagram of the Coexisting Phases (in annealed mixes) in the $\text{MnO-Al}_2\text{O}_3\text{-SiO}_2$ System.

corundum; and (b) spessartite, anorthite, and corundum; anorthite, mullite, and corundum, he concluded that alternative (a) fitted his experimental data; this is not in agreement with the present authors' findings, however. It will be noted that spessartite forms compatible pairs with all but two of the phases which are stable in the system, the exceptions being MnO and mullite.

The equilibrium relationships at the liquidus surface of this system are very complex, and much more experimental data would be necessary to establish with certainty the areas of the fields of primary crystallization and the invariant points. As indicated by Snow, the fields of tridymite, cristobalite, mullite, and corundum probably occupy more than two-thirds of the $\text{MnO-Al}_2\text{O}_3\text{-SiO}_2$ system, and, with the exception of the manganese anorthite field, the present evidence confirms Snow's diagram. Manganese anorthite appears to be a stable compound, melting congruently with a field of primary crystallization surrounding the point representing its composition in the diagram, but the results are not sufficiently numerous to establish the extent of the field accurately. Evidence was not obtained to justify a field of stability for manganese cordierite on the liquidus surface.

The manganese anorthite area is of particular importance in the study of non-metallic inclusions, especially those introduced by the reaction of the

(8) Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$).

(9) Silica, in the form of cristobalite or tridymite.

According to McIntosh, Rait, and Hay,²⁶ the compound $3\text{FeO} \cdot \text{Al}_2\text{O}_3$ is formed below the temperature of liquid formation in the system $\text{FeO}-\text{Al}_2\text{O}_3$, the main evidence being that the spinel crystals showed an altered zone. However, White¹ has pointed out that as the reduction curves of Schenck, Franz, and Willeke²⁷ give no indication of the occurrence of this compound at 800° or 900° C., but indicate that $\text{FeO} \cdot \text{Al}_2\text{O}_3$ (containing a certain proportion of Fe_3O_4 in solid solution) may be stable in contact with metallic iron, a certain degree of reaction between separating solid and residual liquid during freezing would be expected, and this would account for the apparently altered zone in some of the $\text{FeO} \cdot \text{Al}_2\text{O}_3$ crystals.

The foregoing phase data cover the inclusions arising from deoxidation and from the reaction of manganese in the steel with the firebrick casting-pit refractories. The identification of trapped slag and the reaction products of slag and refractories calls for a knowledge of the more complex systems containing CaO and MgO.

THE SYSTEM $\text{CaO}-\text{MgO}-\text{SiO}_2-\text{Al}_2\text{O}_3$.

Although the quaternary system has not yet been thoroughly worked out, much useful data can be obtained from a consideration of the four bounding ternary systems, $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$,^{11, 15} $\text{MgO}-\text{SiO}_2-\text{Al}_2\text{O}_3$,^{28, 15} $\text{CaO}-\text{MgO}-\text{SiO}_2$,^{29, 30, 31, 32} and $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3$.³⁴

The quaternary system is of considerable complexity. Two binary solid-solution series occur, namely the pyroxene series between clino-enstatite ($\text{MgO} \cdot \text{SiO}_2$) and diopside ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$), described by Bowen,³⁵ and the melilite series between akermanite and gehlenite, the thermal equilibrium diagram of which was determined by Ferguson and Buddington.³⁶ According to McCaffery, Oesterle, and Schapiro,³⁷ one quaternary compound, madisonite ($2\text{CaO} \cdot 2\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$), occurs, but Parker and Ryder³⁸ obtained no confirmation of the occurrence of a quaternary compound in a more recent investigation. Recent work by Rait³⁹ has shown that the phase distribution proposed by McCaffery, Oesterle, and Schapiro requires modification, the phase distribution in part of the system being as follows:

- (a) CaO , MgO , $3\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$.
- (b) $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, MgO .
- (c) $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, MgO .
- (d) $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, MgO .
- (e) $3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, MgO .

- (f) $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$, $2\text{MgO} \cdot \text{SiO}_2$, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, MgO .
- (g) $2\text{CaO} \cdot \text{SiO}_2$, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, MgO .
- (h) $2\text{CaO} \cdot \text{SiO}_2$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$.
- (i) $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$.
- (j) $2\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, $2\text{CaO} \cdot \text{Al}_2\text{O}_3$, SiO_2 , $3\text{CaO} \cdot 2\text{SiO}_2$.
- (k) $2\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, $\text{CaO} \cdot \text{SiO}_2$.
- (l) $3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, $\text{MgO} \cdot \text{SiO}_2$.
- (m) $3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$.

In the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system, there is another ternary compound, anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), which is a likely constituent of non-metallic inclusions, but it is interesting to note that grossularite garnet ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) is not found. Gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) melts congruently at 1590° C., crystallizes as clear grains, and belongs to the tetragonal system (optical properties: $\omega = 1.669$, $\epsilon = 1.658$, uniaxial negative). Anorthite melts congruently at 1535° C. and belongs to the triclinic plagioclase-felspar isomorphous series, a feature of which is multiple twinning.

$\text{MgO} \cdot \text{Al}_2\text{O}_3$ (spinel) belongs to the cubic spinel group of minerals, being isomorphous with hercynite ($\text{FeO} \cdot \text{Al}_2\text{O}_3$) and galaxite ($\text{MnO} \cdot \text{Al}_2\text{O}_3$). It melts congruently at 2135° C., and exhibits the characteristic property of the spinels in dissolving a considerable amount of alumina while retaining its spinel structure, the lattice spacing decreasing progressively with increasing Al_2O_3 content. There is a eutectic between this solid solution and alumina. Structurally, the spinels are regarded as mixed oxides and the calcium aluminates as true oxygen salts; hence there is no solid solubility between the spinels and calcium aluminates.

Forsterite ($2\text{MgO} \cdot \text{SiO}_2$) belongs to the orthorhombic group of minerals, being isomorphous with fayalite ($2\text{FeO} \cdot \text{SiO}_2$) and tephroite ($2\text{MnO} \cdot \text{SiO}_2$).

Monticellite ($\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$) has a modified olivine structure and can dissolve about 10% of forsterite, but is not appreciably soluble in either forsterite, merwinite, or $2\text{CaO} \cdot \text{SiO}_2$.

$\text{MgO} \cdot \text{SiO}_2$ belongs to the pyroxene group of minerals, existing as monoclinic clino-enstatite at high temperatures and transforming to the orthorhombic form, enstatite, on cooling below 1145° C.

Clino-enstatite and diopside ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$) form a complete monoclinic pyroxene series of solid solutions.

The solid-solution ranges in α - and β -wollastonite ($\text{CaO} \cdot \text{SiO}_2$) have recently been established by Bowen and Schairer.⁴⁶

The constitution of basic electric-furnace tapping slags and their reaction products with firebrick refractories may be deduced from these phase combinations, as will be shown later.

COMPLEX SYSTEMS CONTAINING CaO , MgO ,
 FeO , MnO , SiO_2 , AND Al_2O_3 .

According to the recent review by White,¹ there are few data, beyond isolated observations, on the more complex systems, but it is to be expected that a feature of such systems will be the occurrence of solid-solution series in which the basic oxides (FeO , MnO , CaO , and MgO) will be mutually replaceable by one another, so that "mixed" orthosilicates, metasilicates, spinels, &c., containing up to four basic oxides will be formed. The necessary conditions for solid-solution formation of this type are (a) that the crystal structures of the pure end-members of the series should be similar and (b) that the sizes of the substituted ions should not differ widely.

The basic oxides CaO , FeO , MnO , and MgO have the NaCl type of cubic lattice, but a continuous solid-solution series does not exist, because of large differences in the ionic sizes. MgO and FeO are completely soluble in each other, the radii of the cations being 0.78 and 0.83 Å, respectively (*i.e.* differing only by 6.4%), while CaO is immiscible with MgO and FeO in the solid state because the radius of the Ca ion (1.06 Å) is much greater than that of Mg or Fe . FeO and MnO are only partially soluble in each other, and it is to be expected that CaO and MnO are soluble in each other to an even less extent.

The orthosilicates fayalite ($2\text{FeO} \cdot \text{SiO}_2$), tephroite ($2\text{MnO} \cdot \text{SiO}_2$), and forsterite ($2\text{MgO} \cdot \text{SiO}_2$), which are all orthorhombic and belong to the olivine group of minerals, appear to be truly isomorphous and completely soluble in each other in all proportions. The minerals knebelite ($\text{FeO} \cdot \text{MnO} \cdot \text{SiO}_2$), picrotephroite ($\text{MgO} \cdot \text{MnO} \cdot \text{SiO}_2$), and chrysolite ($\text{MgO} \cdot \text{FeO} \cdot \text{SiO}_2$), are members of this olivine series. The relationships between them and the corresponding lime compound, $2\text{CaO} \cdot \text{SiO}_2$, are complicated by the fact that the latter can exist in three allotropic modifications α , β , and γ . According to White,¹ $2\text{CaO} \cdot \text{SiO}_2$ can be only partly soluble in the olivine solid solutions, since there is immiscibility between it and monticellite ($\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$), lime-iron olivine ($\text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2$), and glaucophroite ($\text{CaO} \cdot \text{MnO} \cdot \text{SiO}_2$); monticellite is only partially soluble in forsterite. There is complete miscibility between $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$, $\text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2$, and $\text{CaO} \cdot \text{MnO} \cdot \text{SiO}_2$. Recently the isomorphous compounds merwinite ($3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$),^{30, 31, 32} and the manganese analogue of merwinite ($3\text{CaO} \cdot \text{MnO} \cdot 2\text{SiO}_2$)³² have been identified. On the basis of ionic radii, it is almost certain that the compound $3\text{CaO} \cdot \text{FeO} \cdot 2\text{SiO}_2$, isomorphous with the merwinite, will exist. The attempt by White¹ to depict the homogeneity limits of the "quaternary" orthosilicates should be accordingly modified to include the merwinites;

FeO and MnO cause a closing of the gap between the monticellites and the olivines.

The metasilicates belong to the pyroxene group of minerals. Rhodonite ($\text{MnO} \cdot \text{SiO}_2$) is triclinic, $\text{MgO} \cdot \text{SiO}_2$ exists as monoclinic clino-enstatite at high temperatures but transforms to the orthorhombic form, enstatite, on cooling below 1145° C., while $\text{CaO} \cdot \text{SiO}_2$ exists as monoclinic pseudowollastonite or $\alpha\text{-CaO} \cdot \text{SiO}_2$ above 1150° C., and as triclinic wollastonite or $\beta\text{-CaO} \cdot \text{SiO}_2$ below that temperature. At least three different solid-solution series, orthorhombic, monoclinic, and triclinic, are possible, and relationships in the silicate systems higher than ternary can be of considerable complexity. The orthorhombic series is represented by the enstatite-" $\text{FeO} \cdot \text{SiO}_2$ " solid solutions, which include the mineral hypersthene ($\text{MgO} \cdot \text{FeO} \cdot 2\text{SiO}_2$). Orthorhombic solid solutions will be formed at suitable temperatures over at least part of the composition range of which $\text{MgO} \cdot \text{SiO}_2$ is an end-member. The monoclinic series includes the clino-enstatite-" $\text{FeO} \cdot \text{SiO}_2$ " and the clino-enstatite-diopside series, the hedenbergite ($\text{CaO} \cdot \text{FeO} \cdot 2\text{SiO}_2$) series, and johannsenite ($\text{CaO} \cdot \text{MnO} \cdot 2\text{SiO}_2$). According to White,¹ the triclinic series appears to be the one most commonly represented in acid slags. It includes $\beta\text{-CaO} \cdot \text{SiO}_2$, rhodonite, bustamite ($\text{CaO} \cdot \text{MnO} \cdot 2\text{SiO}_2$), and vogtite (lime-iron-manganese metasilicate containing about 15% of CaO). The solubilities of this triclinic series have been tentatively represented by White. There is a gap separating the wollastonite-bustamite and vogtite series from that of which the "iron rhodonites" and pyroxmangite are members.

Tentative phase diagrams of the systems MgO-MnO-FeO-SiO_2 and CaO-MnO-FeO-SiO_2 have been put forward by White.¹ The diagrams hold for a temperature of 960° C., at which $2\text{CaO} \cdot \text{SiO}_2$ is in the β form, and " $\text{FeO} \cdot \text{SiO}_2$ " will form triclinic wollastonites with $\text{CaO} \cdot \text{SiO}_2$, and orthorhombic pyroxenes with $\text{MgO} \cdot \text{SiO}_2$. In the MgO-MnO-FeO-SiO_2 diagram, complete miscibility of the orthosilicates is assumed, but a gap is shown in the metasilicate series separating the fields of the orthorhombic and triclinic pyroxenes.

The constitution of acid open-hearth finishing slags can be worked out with the aid of these data. Such slags, with their low lime content, consist of about 95% of $\text{FeO} + \text{MnO} + \text{SiO}_2$ and, accordingly, their constitution can be derived from the ternary system FeO-MnO-SiO_2 . Finishing slags are usually saturated with silica and contain up to 55% of SiO_2 . In the slowly cooled condition they consist of primary crystals of silica in a silicate matrix, usually of the fayalite-tephroite series. Whiteley and Hallimond²⁴ found that rhodonite appeared in such slags when the MnO/FeO ratio exceeded 27 : 73. The influence

of lime additions on the constitution of acid finishing slags may be deduced from White's tentative diagrams. Up to 7.8% of CaO the lime goes into solid solution in the silicates, but when the lime content is increased further, vogtite appears, as found by Whiteley and Hallimond. Regarding the minor constituents, it is considered¹ that MgO occurs in both the normal silicates and vogtite if sufficient CaO is present to give this constituent. The addition of Al_2O_3 to CaO-free FeO-MnO-SiO₂ slags of high SiO₂ content should lead to the formation of spinel before mullite. This spinel will presumably contain MnO as well as FeO, and also any Fe₂O₃ which may be present. When CaO is also present, the addition of alumina should lead to the appearance of anorthite, possibly associated with spinel if the ratio of CaO to the other bases is low, but without spinel—except possibly magnetite—if this ratio is high. In the quaternary system CaO-FeO- Al_2O_3 -SiO₂, the phase assemblages occurring in the solid slag would be: Tridymite-olivine-anorthite-hercymite, tridymite-wollastonite (metasilicate solid-solution series)-olivine-anorthite, and tridymite-wollastonite (metasilicate solid-solution series)-anorthite.

Owing to the inadequacy of the data, it is difficult to deduce the constitution of the products of reaction between acid slag and firebrick. However, it is well known that the corrosive action of acid slag on firebrick ladle linings is very much less severe than that of basic slag, and few inclusions of this type are to be expected.

THE CONSTITUTION OF NON-METALLIC INCLUSIONS.

The constitution of non-metallic inclusions was elucidated by the application of the available phase-diagram data, X-ray powder examination of mechanically extracted inclusions, X-ray and chemical analyses of residues, and microscopic examination. Spectrographic methods were also used, but without much success.

The examples studied are divided into two categories:

- (a) Non-metallic inclusions in alloy steel cast as uphill-poured ingots.
- (b) Non-metallic inclusions in alloy steel cast as top-poured ingots.

Inclusions in Uphill-Poured Steel.

In an earlier investigation, Rait² found that light nickel-chromium-molybdenum steel forgings made from 11-in. ingots which had been uphill-cast over siliceous firebrick refractories (containing about 25-30% of Al_2O_3) had low transverse elongations, whereas similar forgings made from identical ingots poured uphill over more aluminous firebrick refractories (containing about

38% of Al_2O_3) had completely satisfactory transverse elongations. In the former case, striated fractures were obtained (see Fig. 24), which indicated the presence of harmful inclusions in the test-piece. The shape and general characteristics of these inclusions are shown in Fig. 26, and the chief features of this investigation will be summarized for the purpose of continuity. McCance,⁴⁰ in discussing the manganese-silicon equilibrium in steel, has indicated the influence of this equilibrium on the cleanness of steel during uphill teeming, and has suggested that if the steel contains more manganese than equilibrium conditions require, the manganese will

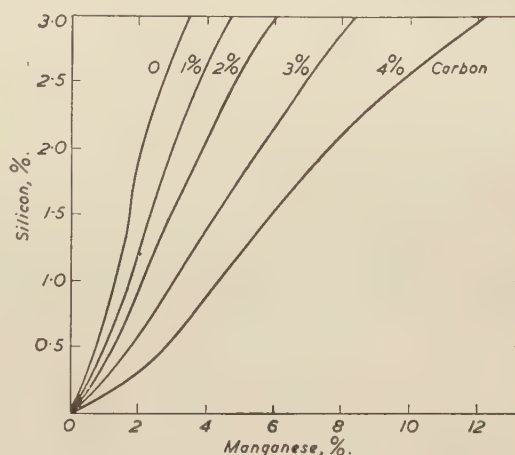
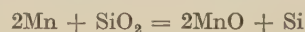


FIG. 87.—Mn-Si Equilibrium Curves (according to Körber).

attack the firebrick, thus introducing non-metallic inclusions. He also suggested that small additions of aluminium would suppress this reaction and thus considerably reduce the amount of inclusions due to slagged refractory.

The reduction of silica by manganese was studied by Krings and Kehren⁴¹ and later by Körber,⁴² the reaction taking place being:



and for equilibrium:

$$K_{\text{MnSi}} = \frac{[\text{Mn}]^2(\text{SiO}_2)}{(\text{MnO})^2[\text{Si}]}$$

where

[Mn] = concentration of manganese in the steel.

(MnO) = concentration of MnO in the slag.

[Si] = concentration of silicon in the steel.

(SiO₂) = concentration of silica in the slag.

The equilibrium amounts of manganese and silicon for different carbon contents are illustrated in Fig. 87, which shows that the amount of silicon in equilibrium with a given content of manganese is reduced as carbon increases. As the heat balance of this reaction is small, the variation of the

equilibrium constant with temperature is also small (*see* Table III.), being given by the equation :

$$\text{Log } K_{\text{MnSi}} = \frac{3.177}{T} - 4.757.$$

Since most steels contain more manganese than equilibrium conditions require, the manganese reduces the available silica of the firebrick refractory material in an endeavour to attain equilibrium. The MnO thus formed fluxes the

TABLE III.—Variation of K_{MnSi} with Temperature.

Temp., ° C.	K_{MnSi}
1650	$7.8_5 \times 10^{-4}$
1600	$8.6_9 \times 10^{-4}$
1550	$9.6_8 \times 10^{-4}$
1500	$10.8_4 \times 10^{-4}$
1450	$12.2_2 \times 10^{-4}$

alumino-silicate refractory to form low-melting slag. The more siliceous refractories had a thick layer of dark-green, glassy slag adhering closely to the surfaces, particularly on the top inside surface of the runner bricks, indicating that the slag, washed off the refractories, floats on top of the steel. In contrast, the more aluminous refractories were very slightly attacked, only a very thin scale-like layer of slag being found on the attacked surfaces. Typical examples of the two types of slagged refractories and the appearance of corresponding steel cores from the runner channels are shown in Figs. 27 to 30.

The analyses of the slags produced on the uphill-casting refractories, given in Table IV., revealed the following notable features :

(1) The slags consist chiefly of MnO, SiO₂, and Al₂O₃, indicating that the refractories have been fluxed with MnO. In all cases the iron oxide contents are very low and may be accounted for by the iron oxide contents of the refractories.

(2) The slags obtained from the same type of refractory material are all very similar, although the steels investigated varied in carbon content between 0.26 and 0.56%, and in alloying constituents such as nickel, chromium, and molybdenum, but were very similar in manganese content and Mn/Si ratio.

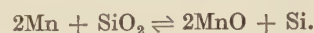
(3) The SiO₂/Al₂O₃ ratio is lower in the slag than in the brick from which it is formed, as shown in Table V.

Evidently the manganese of the liquid steel preferentially reduces silica in the firebrick, forming MnO, which in turn fluxes the refractory to form a slag consisting chiefly of MnO, SiO₂, and Al₂O₃. If the attack were due to residual

MnO in the steel, there would be no reduction in the SiO₂/Al₂O₃ ratio.

The reaction takes place in two stages :

(1) The manganese reacts preferentially with the silica to form MnO and Si according to the equation :



(2) The MnO thus formed fluxes the alumino-silicate refractory to form a manganese alumino-silicate slag.

Since the solubilities of the two types of refractories are very similar—as proved by the similar MnO contents of the slags formed on them, and by the MnO–firebrick fusion curves (Fig. 88)—it was concluded that the great reduction in the amount of slag formed in the more

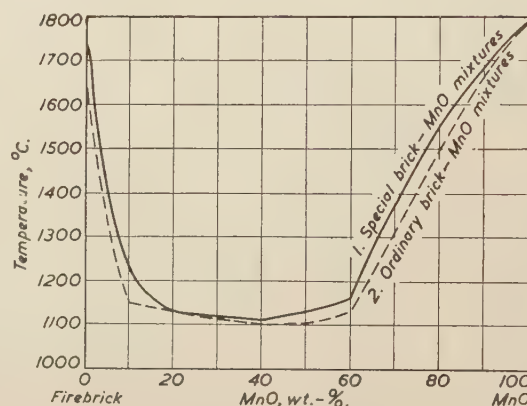


Fig. 88.—Initial Softening Temperatures of MnO–Firebrick Mixtures.

aluminous refractories was due to a great decrease in the amount of MnO formed. Since the only difference in the constitution of the two types of refractories was in the quartz content (*see* Table VI.), it was concluded that quartz is readily reduced by manganese, and that cristobalite and the silica combined in mullite are reduced to a much lesser extent.

The manganese alumino-silicate slag which is in the liquid state at the teeming temperature is washed off the runner bricks and carried into the ingots, as illustrated by Fig. 79. The fractures of the pipes at the bottom of the ingots revealed glassy beads when the steel had been poured through the more siliceous runners, but the steel in the more aluminous channels was found to have smooth surfaces (*see* Figs. 29 and 30), and glassy beads were seldom visible. The inclusions extracted by the Dickenson method from the steel in the runner channels of four casts (*see* Table VII.) consist chiefly of MnO, SiO₂, and Al₂O₃, and are obviously closely related to the slags formed on the uphill-casting refractories. Further evidence that the manganese alumino-

TABLE IV.—*Analyses of Slags Formed on Uphill-Casting Refractories.*

Cast No.	Material.	Analysis of Slag, %.								Analysis of Steel, %.								Casting Temp., °C. (Observed optical, uncorrected).	
		SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	TiO ₂ .	CaO.	MgO.	Alk.	MnO.	C.	Mn.	Si.	Ni.	Cr.	Mo.	S.	P.	Start.	Finish.
1	Refractory	58.1	26.2	5.80	1.20	n.d.	n.d.	n.d.	...										
		63.3	27.2	5.76	1.13	0.44	n.d.	n.d.	...										
		60.0	29.8	6.40	1.13	0.80	n.d.	n.d.	...										
	Slag	54.1	29.6	4.64	1.20	0.88	n.d.	n.d.	8.5	0.28	0.51	0.20	2.85	0.66	Some present.	0.030	0.028	1,420	1,410
2	Refractory	60.2	29.7	6.40	1.30	0.40	1.63	1.94	...										
		56.9	34.5	5.44	1.30	0.60	1.52	2.04	...	0.31	0.61	0.19	2.87	0.60	"	0.039	0.030	1,430	1,420
		54.0	28.3	3.84	1.10	n.d.	n.d.	n.d.	10.8										
	Slag	43.8	30.7	8.32	1.20	n.d.	n.d.	n.d.	12.9										
3	Refractory	57.8	32.6	5.60	1.30	0.60	1.48	n.d.	...										
		60.6	29.3	6.08	1.20	n.d.	n.d.	n.d.	...	0.29	0.62	0.16	2.70	0.70	"	0.036	0.031	1,435	1,430
		45.5	30.1	6.80	1.20	n.d.	n.d.	n.d.	12.7										
	Slag	53.8	28.6	5.12	1.10	n.d.	n.d.	n.d.	10.4										
4	Refractory	57.4	32.7	5.76	1.20	0.60	1.38	n.d.	...	0.28	0.52	0.28	2.68	0.63	"	0.033	0.029	1,430	1,430
		47.0	25.0	7.36	1.00	n.d.	n.d.	n.d.	16.8										
		47.8	27.2	4.48	1.10	16.7										
5	Refractory	58.0	32.5	5.76	1.10	0.80	1.34	n.d.	...	0.28	0.62	0.26	2.66	0.61	"	0.044	0.031	1,430	1,415
		43.4	27.4	4.48	1.10	n.d.	n.d.	n.d.	15.1										
6	Refractory	57.2	33.1	5.92	1.44	0.18	1.27	n.d.	...	0.27	0.56	0.27	2.55	0.58	"	0.028	0.026	1,440	1,430
		52.6	25.8	4.00	0.80	0.70	1.09	n.d.	14.1										
7A	Refractory	57.8	31.5	6.08	1.30	0.70	1.34	n.d.	...	0.30	0.54	0.20	2.75	0.65	"	0.030	0.037	1,430	1,430
		46.4	27.0	4.16	1.10	0.90	1.48	n.d.	18.9										
8	Refractory	55.1	36.4	4.64	1.30	0.90	1.24	n.d.	...	0.28	0.51	0.25	2.66	0.62	"	0.036	0.030	1,460	1,455
											
9	Refractory	52.6	39.2	4.00	1.40	0.80	1.38	n.d.	...	0.29	0.50	0.23	2.65	0.61	"	0.033	0.027	1,425	1,420
		42.4	33.1	3.52	1.40	0.40	1.30	n.d.	16.4										
10	Refractory	53.8	38.2	4.00	1.40	0.60	1.19	2.25	...	0.26	0.48	0.22	2.25	0.64	"	0.028	0.024	1,455	1,445
		45.8	32.3	3.68	1.40	0.50	1.30	n.d.	13.0										
11	Refractory	53.7	37.7	3.36	1.30	0.80	1.23	n.d.	...	0.26	0.47	0.28	2.57	0.65	"	0.032	0.026	1,445	1,440
		44.8	33.4	3.52	1.30	0.50	1.38	n.d.	14.4										
12	Refractory	52.6	38.5	4.00	1.30	0.60	1.09	n.d.	...	0.28	0.56	0.28	2.83	0.56	"	0.028	0.025	1,420	1,410
		44.4	33.2	3.68	1.20	0.20	1.01	n.d.	14.5										
7B	Refractory	53.4	38.1	4.16	1.50	0.80	1.19	n.d.	...	0.30	0.54	0.20	2.75	0.65	"	0.030	0.037	1,430	1,430
		41.7	34.1	3.36	1.20	0.90	1.38	n.d.	18.1										
13	Refractory	53.9	38.1	4.80	1.30	0.90	1.41	n.d.	...	0.29	0.47	0.23	2.72	0.66	"	0.030	0.028	1,440	1,430
		43.8	34.4	4.00	1.20	0.70	1.41	n.d.	15.0										
14	Refractory	53.0	38.1	4.96	1.30	0.90	1.41	n.d.	...	0.28	0.49	0.23	2.54	0.62	"	0.031	0.026	1,430	1,420
		43.4	33.9	4.16	1.20	1.00	1.34	n.d.	15.7										
15	Refractory	54.2	37.5	4.08	1.20	n.d.	n.d.	n.d.	...	0.27	0.50	0.20	2.77	0.62	"	0.033	0.030	1,430	1,420
		43.0	32.9	4.00	1.10	n.d.	n.d.	n.d.	15.7										
16	Refractory	54.9	37.3	3.92	1.40	6	0.30	0.70	0.34	2.64	0.65	"	0.019	0.018
		42.3	34.2	3.68	1.30	16.0										
17	Refractory	56.5	35.6	4.16	1.10	0.60	1.09	0.27	0.59	0.23	2.57	0.61	"	0.028	0.028
		45.8	31.0	3.68	1.00	1.20	1.34	...	15.1										
18	Refractory	56.7	35.0	3.68	1.20	0.70	1.27	0.27	0.45	0.23	2.61	0.61	"	0.028	0.030
		49.0	30.6	3.52	1.00	1.20	1.30	...	13.0										
19	Refractory	57.0	34.4	4.16	1.10	0.29	0.61	0.23	2.79	0.66	"	0.028	0.023
		46.9	30.5	3.44	0.70	16.9										

n.d. = not determined.

[Continued overleaf.]

TABLE IV.—(Continued).

Cast No.	Material.	Analysis of Slag, %.								Analysis of Steel, %.								Casting Temp., ° C. (Observed optical, uncorrected).	
		SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	TiO ₂ .	CaO.	MgO.	Alk.	MnO.	C.	Mn.	Si.	Ni.	Cr.	Mo.	S.	P.	Start.	Finish.
20	Refractory	56.5	34.7	4.00	1.00	0.30	0.62	0.21	2.82	0.67	Some present.	0.023	0.019
	Slag	43.7	33.6	3.84	1.10	15.5										
21	Refractory	56.5	34.3	4.52	1.10	0.28	0.55	0.23	2.90	0.73	..	0.031	0.014
	Slag	48.3	32.7	3.52	1.00	13.2										
22	Refractory	56.8	34.4	4.00	1.10	0.28	0.69	0.23	2.77	0.65	..	0.016	0.019
	Slag	43.3	31.4	3.28	1.00	17.3										
23	Refractory	55.4	35.4	4.48	1.00	0.30	0.58	0.18	2.70	0.63	..	0.019	0.019
	Slag	44.4	32.5	3.44	0.90	15.9										
24	Refractory	56.5	35.5	4.16	1.30	0.32	0.68	0.28	2.77	0.71	..	0.016	0.019
	Slag	43.4	33.8	3.20	1.20	15.3										
25	Refractory	54.9	30.3	6.08	1.10	0.90	1.23	0.30	0.70	0.34	2.64	0.65	..	0.019	0.018
	Slag	43.8	26.2	4.16	0.70	2.30	1.19	...	21.4										
26	Refractory	57.3	31.6	6.56	1.20	0.41	0.64	0.24	3.41	0.08	...	0.033	0.053
	Slag	35.5	39.1	3.84	1.25	18.1										
27	Refractory nest 1	58.0	31.9	5.76	1.20										
	" 5	57.5	32.0	5.98	1.20	0.39	0.61	0.28	3.36	0.06	...	0.038	0.042
	Slag nest 1	40.0	35.7	3.68	1.10	17.8										
	" 5	44.9	31.1	4.00	1.00	16.9										
28	Refractory	56.5	32.8	5.44	1.00	0.38	0.52	0.24	3.44	0.01	...	0.038	0.034
	Slag	45.3	32.4	3.52	0.70	16.9										
29	Refractory nest 1	57.3	32.4	5.76	1.20										
	" 2	58.1	31.6	5.84	1.20										
	" 3	57.6	32.5	5.80	1.15										
	" 4	56.9	33.1	5.76	1.20										
	" 5	58.3	31.1	5.80	1.30	0.53	0.55	0.23	...	0.06	...	0.037	0.035
	Slag nest 1	44.0	31.7	3.36	1.10	18.3										
	" 2	45.3	31.5	4.00	1.15	16.0										
	" 3	44.0	32.7	3.52	1.20	16.8										
	" 4	45.4	31.9	3.84	1.10	16.5										
	" 5	50.6	29.0	3.52	1.08	14.1										
30	Refractory	58.2	32.0	5.65	1.15	0.53	0.57	0.24	...	0.13	...	0.043	0.030
	Slag	50.2	30.0	4.00	0.80	0.50	1.19	...	12.2										
31	Refractory	57.0	34.0	5.12	1.00	0.56	0.57	0.26	...	0.04	...	0.040	0.033
	Slag	41.6	39.0	4.80	0.70	12.0										
32	Refractory nest 1	57.3	33.1	5.84	1.10										
	" 2	53.4	33.3	4.08	1.30	0.85	1.74	0.29	...	0.15	...	0.030	0.038
	Slag nest 1	38.8	30.5	2.40	1.00	25.5										
	" 2	32.8	36.1	2.96	0.90	24.9										

silicate inclusions were retained in the steel was obtained by extracting (by means of the Dickenson method) the inclusions from each end of three forgings which failed on the transverse elongation test (see Table VIII.). There is a marked reduction in the amount of these manganese aluminosilicate inclusions when the steel is poured through the more aluminous refractories.

Since the only difference in the production of the various casts for these forgings was in the type of uphill-casting refractories employed, it can only be concluded that some of the manganese aluminosilicate is trapped in the ingots

and that the amount of slag formed on the refractories and retained in the steel is greater when the more siliceous refractories are used. Since the temperature during forging falls from about 1230° to about 950° C., these manganese aluminosilicates are in the plastic state and are elongated into stringers parallel to the grain flow (see Fig. 26). It should be noted that all these acid open-hearth casts were uphill-poured through magnesite nozzles into 11-in. ingots and that no additions of aluminium were made. Hence, if the inclusions are proved to contain alumina, it is certain that they have been derived from firebrick refractories.

TABLE V.— $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio in Refractories and Slags.

Cast No.	Ratio (Refractory).	Ratio (Slag).
1	2.18	1.83
2	2.02	1.90
	1.62	1.43
3	1.77	1.51
	2.06	1.88
4	1.75	1.76
5	1.79	1.77
6	1.69	2.00
7A	1.83	1.71
8
9	1.34	1.28
10	1.41	1.41
11	1.42	1.34
12	1.36	1.32
7B	1.40	1.22
13	1.41	1.27
14	1.38	1.28
15	1.44	1.31
16	1.47	1.23
17	1.58	1.48
18	1.62	1.60
19	1.65	1.53
20	1.63	1.30
21	1.64	1.47
22	1.65	1.37
23	1.56	1.36
24	1.59	1.28
25	1.81	1.67
26	1.81	0.91
27	1.82	1.12
	1.80	1.44
28	1.72	1.40
	1.77	1.38
	1.84	1.43
29	1.77	1.34
	1.72	1.42
	1.87	1.74
30	1.82	1.67
31	1.67	1.07
32	1.73	1.27
	1.39	0.91

Furthermore, inclusions found on the surfaces of those ingots uphill-poured through the more siliceous refractories proved to be manganese aluminosilicates, the analyses of which were similar to those of the slags formed on the refractories by the manganese reaction, and are also similar to the scums found by Houston⁴³ on the surfaces of uphill-poured tyre-steel ingots (see Table IX.).

TABLE VI.—Calculated Constitution of Uphill-Casting Refractories.

Refractory.	Composition, %.			Total "Free Silica."
	Mullite.	Cristobalite.	Quartz.	
Ordinary	39.2	22.0	13.5	35.5
Aluminous	47.0	26.4	0.3	26.7

As MnO , SiO_2 , and Al_2O_3 comprise more than 90% of the total oxides in these slags, and the contents of the remaining oxides are somewhat similar for the various slags, their constitutions may be considered on the basis of the system $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3$. Accordingly their compositions have been recalculated on this ternary basis (Table X). These compositions fall within the ternary mullite field. On cooling rapidly from steelmelting temperatures, the slags will either freeze to amorphous glasses or the crystallization will be arrested, resulting in the formation of mullite crystals embedded in a glassy matrix. Unfortunately, only a few of these slags were retained for X-ray examination, but the constitutions, given below, agree with the above deductions.

Cast No.	Constitution (X-Ray).
14	Mullite and glass.
3	Mullite, quartz, and glass.
7	Amorphous.
10	Mullite and glass.

Typical Examples of Non-Metallic Inclusions in Uphill-Poured Steel.

Example 1.

Polished sections of runner scrap from the more siliceous runner bricks were examined by the microscope. The inclusions were largely amorphous, but annealing at 900° C. for 50 hr. resulted in devitrification and, after etching with alkaline sodium picrate, crystalline structures such as are shown in Fig. 31 were obtained. X-ray powder analyses of mechanically removed inclusions indicated the presence of manganese anorthite (large), mullite, and cristobalite (small). Similar constitutions were found for the annealed slags scraped from the more siliceous runner bricks. Unfortunately, the inclusions in the forgings were too small for X-ray investigation, but chemical

TABLE VII.—Non-Metallic Inclusions in Runner Scrap (Dickenson Method).

Cast No.	Weight of Inclusions, %.	Analysis, wt.-%.						
		SiO_2 .	Al_2O_3 .	Fe_2O_3 .	TiO_2 .	CaO .	MgO .	MnO .
3	0.037	68.4	28.0	2.80	0.50	0.75	0.81	6.6
4	0.145	59.6	23.4	2.08	0.70	0.40	0.90	11.0
		54.4	32.8	3.38	1.00	0.44	1.09	5.4
10	0.012	50.0	35.0	4.00	1.20	1.60	1.45	7.2
11	0.011	71.8	5.3	3.20	1.80	0.75	0.18	16.7

TABLE VIII.—*Details of Inclusions taken from Faulty Forgings.*

Cast No.	Position in Ingot.	Analysis, %.						Weight of Inclusions, %.	O ₂ (gas analysis), wt.-%.
		MnO.	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	TiO ₂ .	CaO.		
2	Top	9.5	57.9	18.6	0.72	1.0	0.9	0.012	0.009
	Bottom	12.1	63.4	14.8	5.3	1.0	Trace	0.017	n.d.
4	Top	1.3	70.0	24.5	1.6	1.4	0.25	0.012	0.007
	Bottom	1.0	70.3	25.4	1.6	1.3	0.26	0.011	0.009
34	Top	23.8	56.7	15.0	4.26	0.8	0.33	0.016	0.009 ₅
	Bottom	24.8	58.3	13.3	2.44	0.9	0.19	0.015	0.009

n.d. = not determined.

TABLE IX.—*Comparison of Analyses of Certain Ingot Scums.*

Investigator.	Analysis, %.							
	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.
Rait ²	42.30	0.64	26.80	2.24	1.87	23.80	1.40	0.98
	31.60	0.64	35.24	5.12		22.00	2.40	2.09
Houston ⁴³	55.5	...	25.80	...	3.40	13.50	0.30	...
	47.6	...	23.50	...	2.70	25.50	0.60	...

TABLE X.—*Slag Composition, on Basis of System MnO-SiO₂-Al₂O₃.*

Cast No.	Composition.			Cast No.	Composition.		
	MnO, %.	SiO ₂ , %.	Al ₂ O ₃ , %.		MnO, %.	SiO ₂ , %.	Al ₂ O ₃ , %.
1	9.3	58.6	32.1	21	14.1	51.2	34.7
2	11.6	58.0	30.4	22	18.8	47.1	34.1
3	14.4	51.5	34.1	23	17.2	47.8	35.0
4	18.9	52.9	28.2	24	17.7	46.9	35.4
5	16.7	53.2	30.1	16	17.3	45.7	37.0
6	16.4	56.8	26.8	25	23.4	47.9	28.7
7A	20.5	50.3	29.2	26	19.5	38.4	42.1
9	17.9	46.1	36.0	27	19.0	42.8	38.2
10	14.4	50.2	35.4	27	18.2	48.3	33.5
11	15.6	48.4	36.0	28	17.7	48.0	34.3
12	15.8	48.2	36.0	28	19.7	46.8	33.5
7B	19.3	44.4	36.3	28	17.3	48.8	33.9
13	16.1	47.0	36.9	29	18.0	47.1	34.9
14	16.9	46.7	36.4	29	17.6	48.4	34.0
17	17.2	49.1	33.7	29	14.9	54.2	30.9
18	14.7	52.9	32.4	30	13.2	54.3	32.5
19	18.0	49.7	32.3	31	12.9	44.9	42.2
20	16.7	47.1	36.2	32	27.0	40.9	32.1
15	17.2	46.9	35.9	32	26.7	34.9	38.4

extraction (see Table VIII.) has confirmed the similarity of their compositions, and their microstructures (Fig. 32) closely resemble those in the runner sections.

Example 2.

Micro-examination of the polished samples of the steel cast through the more aluminous runners revealed a decreased amount of non-metallics of a type shown in Fig. 33. According to the re-

calculated compositions shown in Table X., the constitution of the non-metallics derived from the more aluminous runner bricks should be mullite, manganese anorthite, and cristobalite, but X-ray analysis of non-metallics mechanically removed from runner scrap and annealed at 900° C. for 50 hr. proved the presence of spessartite and spinel (Fig. 34). Furthermore, slag scraped from the aluminous runner bricks, inserted in a piece of steel and subsequently forged, was found

on X-ray examination to consist of large amounts of mullite and a small amount of spinel of the Fe_3O_4 type (Fig. 35). This confirms the previous evidence that the amount of non-metallics resulting from the uphill-casting refractories is negligible when aluminous firebricks (38% of Al_2O_3) are used. The spessartite-type inclusions must therefore have been produced by the manganese attack on firebrick in some other part of the casting system, such as the ladle or launder lining.

Example 3.

A further interesting example is provided by a heat of nickel-chromium-molybdenum steel similar in composition to the steels previously discussed but made in the basic-electric furnace. A small cake of aluminium (8 oz./ton), weighted with ferromanganese, was added to the bath just before tapping, and the steel was uphill-poured over the more aluminous type of refractories. As in the case of the acid steel, the aluminous refractories were only very slightly attacked. The thin scale-like layer of manganese aluminosilicate slag was found by X-ray powder analysis to consist of mullite (large) and manganese anorthite (medium). Examination of polished sections of the runner metal revealed the absence of the typical manganese aluminosilicates. Fig. 36 shows a section from the runner metal annealed at 1100°C . for 18 hr. Crystalline phases are present which, according to X-ray powder analysis, are spinel and a pyroxene isomorphous with enstatite. The lattice spacing of the spinel is slightly greater than that of pure $\text{MgO} \cdot \text{Al}_2\text{O}_3$, indicating that the spinel phase consists chiefly of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ with small amounts of iron or manganese in solid solution. The spinel has the appearance of having been partially attacked during annealing. Fig. 37 shows another inclusion found in the runner metal of this cast. The rectangular crystals appear to be spinel and the needles are most probably alumina. It will be noted in a later section that $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel inclusions have been identified in other casts of basic electric-furnace steel in which a cake of aluminium weighted with ferromanganese has been added to the bath just before tapping. It would appear that the cake sinks to the bottom of the bath, and as the alumina is formed it reacts

with the magnesia of the dolomite hearth to form spinel.

Example 4.

A further example found in an open-hearth bottom-run steel of similar composition reveals the presence of a different type of inclusion. Eight ounces of aluminium per ton of steel were added to the ladle. The inclusions appear to be very hard, crystalline, and translucent, and are probably the result of the reaction between aluminium and other inclusions. Portevin and Castro⁴⁴ have reported similar inclusions. A typical example is shown in Fig. 38.

Inclusions in Top-Poured Steel.

The formation of manganese aluminosilicate slags as a result of the manganese attack on firebrick is not confined to uphill-casting refractories. Such slags formed on firebrick tundish linings can usually be observed floating on the surface of the liquid steel. The analyses of the dark-green, glassy slags removed from the tundishes through which a nickel-chromium-molybdenum steel similar in composition to those previously considered has been poured, are shown in Table XI., together with the composition of the firebrick lining.

The compositions (calculated to 100% $\text{MnO} + \text{SiO}_2 + \text{Al}_2\text{O}_3$) of these tundish slags and the slags on the uphill-casting refractories have been plotted in Fig. 89 for comparison. The compositions of the tundish slags lie on the line between MnO and the aluminosilicate composition of the tundish lining. Similarly, the latter slags, which lie within the small shaded area, fall on the line between the composition of the uphill-casting refractories and MnO . Hence the ultimate composition of these manganese aluminosilicate inclusions is largely controlled by the composition of the aluminosilicate refractory from which they are derived. The slags compared in Fig. 89 were formed by the action of steels with similar carbon, manganese, and silicon contents, but with varying contents of alloys; it would appear that the alloy content within the range examined has little influence on the reaction. The compositions of the slags produced on the runner bricks in cast 32 (see Table X.) lie outside the shaded area. This

TABLE XI.—Analyses of Tundish Slags and Refractory Lining (Cast No. 33).

	Composition, %.							
	MnO .	SiO_2 .	Al_2O_3 .	Fe_3O_4 .	Cr_2O_3 .	TiO_2 .	CaO .	MgO .
Tundish No. 1 . . .	30.0	45.3	15.3	6.5	1.37	0.6	0.3	1.2
" No. 2 . . .	29.5	48.2	13.4	5.6	1.32	0.5	0.6	0.7
Refractory lining	69.8	22.6	6.4	...	0.8	n.d.	n.d.

n.d. = not determined.

steel has a higher manganese content and a greater Mn/Si ratio than the others and produces slags richer in MnO. The compositions of these manganese aluminosilicate slags are therefore largely controlled by:

- (1) The original composition of the aluminosilicate refractory from which they are derived.
- (2) The carbon and manganese contents and the Mn/Si ratio of the steel.

The formation of manganese aluminosilicates will not be confined to uphill casting; they will be formed whenever liquid steel comes into contact with aluminosilicate refractory such as compose the launder, ladle lining, stoppers and nozzles, and tundishes. Systematic investigations will be required to establish quantitatively the contributions of each of these sources to the manganese aluminosilicate contents. It is certain,

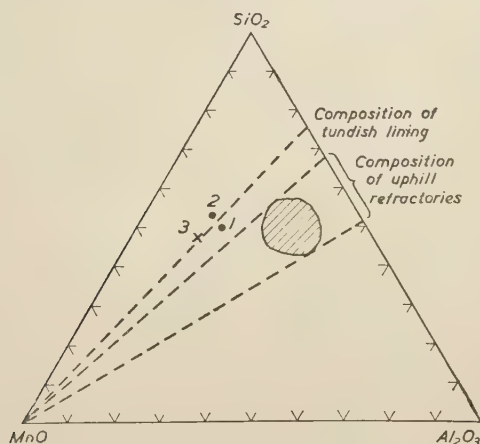


FIG. 89.—Composition of Slags from uphill-casting refractories and tundish linings.

however, that the amounts from each source will be greatly reduced with increasing alumina content of the refractory (*i.e.*, with decreasing quartz content). These sources of inclusions should not be lightly dismissed, because the popular idea that the top-cast ingots are cleaner than uphill-teemed ingots is not always correct.

In the following section the inclusions described are those which have been located in ingots cast singly by top pouring, and in the majority of instances the steel was cast through tundishes. Cast histories of the top-poured ingots from which examples 5, 6, 7, 8, 10, 11, 13, 14, 15, 16, and 21 were taken are given in Table XVI.

Example 5.

This example concerns inclusions located towards the bottom end of a forging made from a 4-ton ingot cast from the basic-electric furnace through a tundish lined with firebrick of similar composition to that shown in Table XI.

The composition of one of these inclusions, described in Table XII., is almost identical with that of the slag formed in the tundish by a similar steel (*see* Table XI.), indicating that the inclusion has been derived from the tundish lining.

TABLE XII.—Composition and Constitution of Inclusion. (Example 5.)

Cast.	Weight, %.	Composition, %.	Constitution (X-Ray).
35	0.010	MnO 35.2 SiO ₂ 43.5 Al ₂ O ₃ 12.8 Fe ₂ O ₃ 6.4 TiO ₂ 1.3 CaO trace	Rhodonite (medium). MnO.Al ₂ O ₃ .2SiO ₂ (medium). Manganese anorthite. Pyroxene (diopside type), large. Fe ₂ O ₃ (small).

The structures of two separate inclusions, found in the same test-piece, are shown in Figs. 39 and 40; both these specimens were etched in boiling alkaline sodium picrate for 5 min. Repolishing, and etching of the inclusion shown in Fig. 39 in a 10% solution of hydrofluoric acid for a minute or two at a time indicated that the long needles were more resistant to attack than the ground mass. Upon continued etching, the needles were eventually removed, although it would be difficult to say whether they were themselves attacked or whether they were removed on account of the removal of the ground mass.

An attempt was made to take glancing-angle X-ray photographs of the inclusions *in situ*, but no positive result was obtained. X-ray analysis of the extracted inclusions, however, revealed the presence of the following phases (*see* Fig. 66(a)):

- (1) Rhodonite (MnO.SiO₂), probably with small amount of "FeO.SiO₂" in solid solution (Mn,Fe)O.SiO₂. (Medium amount.)
- (2) A phase isomorphous with anorthite (CaO.Al₂O₃.2SiO₂), largely MnO.Al₂O₃.2SiO₂. (Medium amount.)
- (3) Monoclinic pyroxene (diopside type of structure).
- (4) Fe₂O₃. (Small amount.)

The detection of manganese anorthite is interesting, and it is believed that this phase appears in Fig. 40, together with pyroxene, in which dendritic octohedra can be seen. Fig. 40 should be compared with Fig. 31, which is a photomicrograph, after etching in alkaline sodium picrate, of an inclusion the X-ray analysis of which showed large quantities of manganese anorthite. Rhodonite is probably present in the form of needles in Fig. 40, and pyroxene and manganese anorthite in the more dendritic form. A small amount of Fe₂O₃ is also present. The composition of the inclusions lies very near to the rhodonite and manganese anorthite fields of crystallization in the system MnO-SiO₂-Al₂O₃.

The monoclinic pyroxene (diopside type) does not occur in the pure $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3$ system; however, it evidently consists largely of MnO and SiO_2 stabilized most probably by the solid solution of small amounts of FeO , CaO , and MgO .

Example 6.

This example concerns an inclusion found towards the bottom end of a similar forging to that mentioned in connection with example 5.

The inclusion, which is not unlike that found in Fig. 40, is shown in Fig. 41. In this instance manganese anorthite and monoclinic pyroxene appear to be present, the former bearing a close resemblance to the manganese anorthite shown in Fig. 31.

Example 7.

This example shows an inclusion which again bears some similarity to that found in example 5.

Fig. 42 is a photomicrograph of this type of inclusion etched in alkaline sodium picrate. The acicular type of constituent, which is readily apparent, appears to be rhodonite. No very definite evidence of the constituents which were thought to be manganese anorthite and monoclinic pyroxene in Fig. 40 can be seen.

Example 8.

This example concerns the finishing slag of an acid open-hearth steel. A final slag sample analysed as follows:

SiO_2 , %.	FeO , %.	MnO , %.	CaO , %.
58.0	15.5	17.5	7.5

A small portion of this slag was powdered and inserted into a bar of carbon steel, forged, annealed, and then examined microscopically. Unetched, a dark constituent was detected, which is shown in Fig. 43. This constituent has an appearance similar to that of tridymite. Subsequent etching in alkaline sodium picrate revealed a second, lighter, constituent, while at the same time the darker constituent was partially attacked. An X-ray photograph of the powder scraped from this inclusion after annealing gave the following constitution:

Tridymite	Large.
Pyroxene	Small.
Olivine (tephroite)	Medium.
„ (fayalite)	

The X-ray photograph of these constituents is shown in Fig. 66(b) and from this there is no doubt that the dark constituent shown in the photomicrograph of the unetched specimen is tridymite. The significance of this result will be seen in the following example.

Example 9.

This example concerns a forging of some 50 cwt. made from basic-electric steel cast through a tundish lined with firebrick. Inclusions were located in a test-piece towards the bottom end. This type of inclusion was dark brown in colour, running almost completely across the tensile test-specimen, which means that its total length was half an inch.

Different parts of the inclusion had quite widely differing appearances. Representative photomicrographs are shown in Figs. 44, 45, and 46. Notable features are the light-coloured crystalline particles in Fig. 45, and the lath-shaped crystals in Fig. 46. The portion of the inclusion shown in Fig. 45 was surrounded by a film of ferrous oxide. Etching tests showed little attack by alkaline sodium picrate or hydrochloric acid (except in the case of the oxide film, which was completely removed). The inclusion was attacked more strongly by hydrofluoric acid.

A spinel is readily seen in the as-polished specimen (Fig. 45), while the dark, crystalline phase in Fig. 46 is a free form of silica which has been shown to be tridymite (see Fig. 43). This inclusion is also unetched; on etching with a 10% hydrofluoric acid solution, however, both the ground mass and the free silica were attacked.

Example 10.

Another inclusion of the same type, from a similar heat and from a similar type of forging, is shown in Fig. 47. Free silica (in the form of tridymite) is again apparent as the darker constituent, while the ground mass would appear to be a complex silicate.

Example 11.

This example concerns inclusions found near the bottom end of a 3-ton forging made from basic-electric steel.

Unetched, the inclusion showed a free constituent of definite crystallinity (almost certainly cristobalite). The corresponding photomicrograph is shown in Fig. 48. Another part of the same inclusion, etched in alkaline sodium picrate, is shown in Fig. 49. The similarity with Fig. 40 is again very striking and it would appear that similar constituents are present, namely rhodonite, manganese anorthite, and monoclinic pyroxene.

Example 12.

This example is of another type of inclusion from the same steel. Free silica (tridymite) was identified in the unetched section, while the background had a duplex structure.

On etching with hydrofluoric acid, the

background was appreciably attacked and the free silica slightly attacked; this is readily observed in Fig. 50. A careful comparison between the unetched and etched sections shows how the background has been attacked in such a manner as to uncover additional free-silica laths. Subsequently this example was repolished and then etched with hydrofluoric acid; a general attack on the ground mass and the free silica was observed.

Example 13.

A unique series of inclusions in one 30-cwt. forging provides this and other examples. The inclusions were found 5 ft. from the top end of the forging and just below the skin. The photomicrograph (Fig. 67) shows the structure of one of these inclusions, unetched. The chief constituent is alumina in the form of laths and crystals. The etched structure, with a background of eutectic appearance, one phase of which appears to be alumina, is shown in Fig. 68.

Example 14.

Figs. 51 and 52 show another inclusion, unetched and etched in alkaline sodium picrate respectively. Spinel, and alumina in the form of laths, are apparent. The background has the appearance of a eutectic, one constituent of which is almost certainly alumina. This was confirmed by the X-ray examination of a mechanically extracted inclusion, which proved the presence of spinel and α -alumina; the spinel had a larger spacing than $\text{MgO} \cdot \text{Al}_2\text{O}_3$, indicating a complex solid solution of the type $(\text{Mg}, \text{Fe}, \text{Mn})\text{O} \cdot (\text{Fe}, \text{Al})_2\text{O}_3$. This is shown in the X-ray photograph, Fig. 66(c). The chemical analysis of this inclusion was:

	%.
SiO_2	5.04
Fe_2O_3	2.09
Al_2O_3	75.90
TiO_2	1.15
MnO	6.36
CaO	3.24
MgO	5.86

A variant of this structure is shown in Figs. 53 and 54, but there no alumina is present. The other pale (etched) constituent has not yet been definitely established, but would appear to be a pyroxene.

Example 15.

This example is of inclusions from the same forging, also near the outside towards the top end. The inclusion unetched is shown in Fig. 61, in which the familiar free silica is shown, and which has now been established as tridymite. Only a minor attack was noted after etching in alkaline sodium picrate and hydrofluoric acid.

Fig. 62 shows the inclusion etched in hydrofluoric acid.

Example 16.

This example is of another interesting inclusion from the same forging. Unetched, no structure is shown; after etching in alkaline sodium picrate, attack was noticed (Fig. 63). The tundish scum taken from a steel of similar composition, *viz.*, nickel-chromium-molybdenum steel, produced similarly to that just discussed, was examined chemically, and the following result obtained:

	%.
SiO_2	43.7
FeO	4.75
Fe_2O_3	0.64
Cr_2O_3	1.72
Al_2O_3	12.96
TiO_2	
MnO	33.00
CaO	0.90
MgO	0.54

This analysis should be compared with the average residue analysis given for example 5, and it will be seen that they are almost identical. The tundish scum was X-rayed without annealing, and although the bulk was amorphous, mullite and cristobalite were detected; after annealing, the part previously amorphous was found to consist almost entirely of rhodonite. An X-ray photograph, showing mullite, cristobalite, and an amorphous constituent, is given (Fig. 66(d)). The same sample, after annealing, is illustrated in Fig. 66(e); the amorphous constituent has recrystallized to form rhodonite. Photomicrographs of these phases are shown in Figs. 55 and 69; Fig. 55 shows the presence of rhodonite, and Fig. 69 shows the mullite quite distinctly. Both specimens had been etched with alkaline sodium picrate. By comparing Fig. 55 with Fig. 63, similarities can be seen which indicate the presence of rhodonite in the latter. Silica and mullite may also be present.

Examples 17, 18, 19, and 20.

The constitutions of a few examples of an unusual type of lime-rich inclusion found in basic-electric steel, but not detected in acid steel, are summarized in Table XIII., which was drawn up from data obtained from X-ray examination of the mechanically removed inclusion. Photomicrographs from examples 18 and 20 are shown in Figs. 56 and 57, respectively; the gehlenite can be easily seen. X-ray photographs from examples 18 and 19 are shown in Figs. 80 and 81, respectively.

The analysis and constitution of the slag formed on the surface of the ladle bricks by the

TABLE XIII.—*X-Ray Examination of a Lime-Rich Type of Inclusion (Basic-Electric Steel).*

Example.	Constitution.	
17	Gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$). Anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). $3\text{CaO} \cdot 2\text{SiO}_2$.	Large. Small. Small.
18	Gehlenite. $3\text{CaO} \cdot 2\text{SiO}_2$. Pyroxene.	Large. Small. Small.
19	Gehlenite. Anorthite.	Large. Small.
20	Gehlenite. $3\text{CaO} \cdot 2\text{SiO}_2$.	Large. Medium.

fluxing action of the basic-electric tapping slag are as follows :

Analysis, wt.-%.	Constitution (X-Ray).
SiO_2 . . . 39.10	Gehlenite. (Large.)
FeO . . . 3.60	Anorthite. (Small.)
Fe_2O_3 . . . 1.12	Pyroxene. (Small.)
Al_2O_3 . . . 12.52	
TiO_2 . . . 0.52	
MnO . . . 0.91	
CaO . . . 32.58	
MgO . . . 7.46	

A photomicrograph of this slag layer, in which typical gehlenite crystals are very prominent, is reproduced in Fig. 78. As the constitution of the inclusions is identical to that of the reaction product of slag and firebrick refractories, it would appear that this reaction is the source of the inclusions.

Rait and Goldschmidt⁴⁵ have shown that the constitution of basic-electric tapping slags, and their change in constitution after being in contact with firebrick refractories (launder, ladle lining, stopper rods, &c.), may be deduced from the diagram of the $\text{CaO-MgO-SiO}_2\text{-Al}_2\text{O}_3$ system. The constitutions of a number of tapping slags and firebricks are reported in Tables XIV. and XV. respectively.

The analysis shows that the slag, in its passage from the furnace into the ladle, has dissolved some alumino-silicate refractory, thus passing into a new phase-field in which gehlenite-akermanite solid solution (melilite) is one of the phases. With a knowledge of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ system, the mechanism of the reaction between the slag and the refractories is simply explained. When a CaO-SiO_2 slag (approximate composition $2\text{CaO} \cdot \text{SiO}_2$) comes into contact with firebrick the first liquid formed will have the composition of the ternary eutectic at 1265°C . At steelmaking temperatures, this liquid will be unsaturated with respect to alumino-silicate and will continue to dissolve it in an attempt to attain equilibrium. However, some of this liquid will be washed into the steel and slag before reaching equilibrium.

TABLE XIV.—*Constitution of Various Tapping Slags.*

Slag.	Chemical Analysis, %.										Constitution, wt.-% (calculated).										Constitution (X-Ray).											
	SiO ₂	FeO.	Fe ₂ O ₃	Al ₂ O ₃	MnO.	CaO.	MgO.	CaF ₂	S.	FeO.	MnO.	MgO.	3CaO.SiO ₂	2CaO.SiO ₂	3CaO.Al ₂ O ₃	MgO.Fe ₂ O ₃	MgO.Al ₂ O ₃	4CaO.Al ₂ O ₃ .Fe ₂ O ₃	CaF ₂	CaS.	3CaO.MgO.2SiO ₂	CaO.MgO.SiO ₂	2CaO.Al ₂ O ₃ .SiO ₂	CaO.SiO ₂	Ratio.	MgO.	3CaO.SiO ₂	α-2CaO.SiO ₂	3CaO.MgO.2SiO ₂	CaF ₂		
A	29.2	0.89	0.32	2.04	0.48	54.20	2.17	6.20	0.27	0.88	0.48	2.17	32.6	47.7	4.87	0.67	6	0.61	2.95	Small	
B	28.6	0.36	0.24	2.00	0.43	60.38	2.21	5.20	0.23	0.36	0.43	2.21	13.0	72.2	4.90	0.73	5.2	0.51	2.10	Small	
C	29.7	1.14	0.40	1.72	0.58	56.48	5.54	3.80	0.62	1.14	0.58	4.76	...	85.1	3.8	1.29	1.90	Small	
D	32.0	0.92	0.18	2.25	0.92	55.5	5.07	3.40	0.15	0.92	0.92	3.68	...	64.0	26.6	0.50	2.40	...	3.4	0.34	43.1	1.73	Small	
E	30.4	0.56	0.18	2.97	0.28	50.00	9.55	6.60	0.33	0.56	0.28	3.05	...	42.1	6.6	0.74	1.64	
E'	32.9	0.48	0.34	5.75	0.60	45.55	11.90	1.30	0.25	0.40	...	0.55	66.6	14.8	15.2	1.38

E' = Same slag in ladle.

E = Slag from furnace.

TABLE XV.—*Constitution of Firebricks.*

Analysis, %.							Constitution (X-Ray).			
SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	TiO ₂ .	CaO.	MgO.	Alk.	Mullite.	Quartz.	Cristobalite.	γ-Al ₂ O ₃ .
58.1	26.2	5.80	1.20	n.d.	n.d.	n.d.	Large.	Large.	Trace.	Some.
60.2	29.7	6.40	1.30	0.40	1.63	1.94	Large.	Large.	Trace.	Some.
57.4	32.7	5.76	1.20	0.60	1.38	n.d.	Large.	Large/ Medium.	Trace.	...
55.1	36.4	4.64	1.30	0.90	1.24	n.d.	Large.	Small.	Some.	...
53.7	37.7	3.36	1.30	0.80	1.23	n.d.	Large.	Trace.	Some.	...
53.0	38.1	4.96	1.30	0.90	1.41	n.d.	Large.	Trace.	Some.	...

n.d. = not determined.

According to the phase diagram, such liquid will crystallize to form chiefly gehlenite, with smaller amounts of anorthite and CaO.SiO₂ or 3CaO.2SiO₂ and CaO.SiO₂. In actual practice the small amount of MgO (usually less than 10%) present in the slag will, to a small extent, affect the composition and temperature of the initial liquid formed. In the majority of cases the MgO will occur in melilite and pyroxene. Hence melilite will be the most prominent phase in such inclusions, the minor phases being anorthite, 3CaO.2SiO₂, or pyroxene. This phase-diagram evidence strongly supports the theory of origin of the gehlenite-rich inclusions described in Table XIII.

Example 21.

The inclusion which forms the subject of this example was found towards the outside, near the top, of the forging containing the inclusions described in examples 13, 14, 15, and 16.

In the unetched specimen, a spinel only was identified, but etching in alkaline sodium picrate revealed the presence of two additional phases (Fig. 70). It seems highly probable that the spinel was of the MgO.Al₂O₃ type, which could have been formed in either of the three following ways:

(a) From a reaction between a finishing slag and the ladle or tundish fireclay refractories as previously discussed.

(b) From a reaction between the composite fireclay-magnesite nozzle and slag washed from the ladle bricks, or mechanical erosion of the nozzle by the slag.

(c) From the oxidation of magnesium contained in the aluminium used for deoxidizing the steel. It should be noted that aluminium containing up to 5.0% of magnesium has been supplied for purposes of deoxidation.

The mechanism of the reaction under (a) has been discussed. As the reaction discussed under (b) is a possible source of inclusions, a composite magnesite-firebrick nozzle through which a similar steel had been cast was examined in detail.

A scraping of slag was taken from the firebrick

portion of the nozzle, and examined. The etched structure is shown in Fig. 58 and in it the similarity with the ground mass of the inclusion is striking. An X-ray photograph of the slags (Fig. 82(c)) revealed the presence of gehlenite (as the major constituent) and diopside. There is little doubt therefore that the light constituent in the inclusion and the slag is gehlenite; this conclusion is strengthened and confirmed by comparing the respective photomicrographs (Figs. 70 and 78). An examination of the edge of the magnesite portion of the nozzle showed the microstructure reproduced in Fig. 65. A spinel is readily identifiable in that microphotograph and, after taking an X-ray photograph (shown in Fig. 82(d)), MgO.Al₂O₃ (spinel), gehlenite, and forsterite were noted, the spinel predominating. The inclusion in this forging therefore could have formed from the slag which had been washed off the ladle bricks reacting with the magnesite portion of the nozzle and finally passing into the steel.

Miscellaneous Examples of Non-Metallic Inclusions.

The following inclusions are interesting examples associated with a variety of miscellaneous problems which have arisen in the course of this investigation.

Example 22.

During investigation of the causes of failure of a certain cast of alloy steel which had proved difficult to drill, inclusions of the type illustrated in Figs. 64 and 71 were encountered. The steel, to which 8 oz. of aluminium per ton had been added in the ladle, was produced in the basic-electric furnace. A residue extraction, using the Dickenson method, was attempted and the following chemical analysis was determined:

	%.
SiO ₂	1.97
Fe ₂ O ₃	3.36
Al ₂ O ₃	80.30
TiO ₂	0.14
MnO	0.50
CaO	Trace
MgO	15.14

TABLE XVI.—*Cast-Histories of Top-Poured Ingots.*

	Example.						
	5.†	6.†	7.	8.	10.	11.†	13, 14, 15, 16, 21.
Analysis :							
Carbon, % . . .	0.28	0.31	0.35	0.54	0.35	0.35	0.34
Manganese, % . . .	0.59	0.58	0.57	0.58	0.63	0.62	0.72
Silicon, % . . .	0.16	0.26	0.33	0.23	0.23	0.41	0.24
Sulphur, % . . .	0.010	0.012	0.016	0.041	0.018	0.015	0.017
Phosphorus, % . . .	0.018	0.017	0.113	0.040	0.015	0.019	0.016
Nickel, % . . .	2.50	3.14	2.96	...	2.95	2.87	3.05
Chromium, % . . .	0.61	0.83	0.79	...	0.79	0.77	0.82
Molybdenum, % . . .	0.62	0.52	0.49	...	0.52	0.43	0.51
Deoxidation :							
Si-Mn, lb./ton . . .	4	5 $\frac{3}{4}$	4	18 $\frac{3}{4}$	5 $\frac{3}{4}$	5 $\frac{3}{4}$	2 $\frac{1}{4}$
Fe-Si (50%), lb./ton	19 $\frac{1}{4}$	21 $\frac{1}{4}$	19 $\frac{1}{4}$	15 $\frac{1}{4}$ *	19 $\frac{1}{4}$	19 $\frac{1}{4}$	19 $\frac{3}{4}$
Aluminium addition, oz./ton . . .	8	8	8	0.62	8	8	8
Slag condition . . .	White, falling.	White, falling.	White, falling.	Normal.	White, falling.	White, falling.	White, falling.
Tapping temp., ° C. (Im- mersion pyrometer)	1607	1623	1650	1630	1606	1630	1635
Casting temp., ° C. . .	1430	1430	1420-1435	1420	1430-1440	1420-1440	1425-1440
Time, casting-chill :	min. sec.	min. sec.	min. sec.	min. sec.	min. sec.	min. sec.	min. sec.
No. 1 Ingot . . .	4 25	4 5	3 45	...	3 35	4 ...	2 15
No. 2 „ . . .	4 55	...	3 40	...	3 50	3 50	...
No. 3 „ . . .	4 45	...	4 5	...	4 15	4 15	...
No. 4 „	4 40	...	3 55	4 35	...

* Fe-Mn.

† Examples 5, 6, and 11 were poured through a tundish.

X-ray powder analysis was also carried out on the residue, and the following phases identified: α - Al_2O_3 ; γ - Al_2O_3 ; spinel of a smaller spacing than, but definitely of, the $\text{MgO}.\text{Al}_2\text{O}_3$ type. The smaller spacing proved to be due to the presence of γ - Al_2O_3 in solid solution, the effect of which is illustrated in Fig. 90.

Assuming a linear variation of lattice parameter with composition, the spinel would correspond to approximately 30% of Al_2O_3 and 70% of MgO . The spacing of the inclusion was found to be 8.020 Å. and the spacing of $\text{MgO}.\text{Al}_2\text{O}_3$ 8.068 Å., while the spacing of γ - Al_2O_3 is 7.91 Å. On plotting these values on a graph (with lattice spacing as ordinate and composition as abscissa) it will be seen that they fall on a straight line. With $\text{MgO}.\text{Al}_2\text{O}_3$ as the basic phase, the decrease in spacing can be explained by the omission of Mg^{++} and O^{--} ions from the lattice positions in $\text{MgO}.\text{Al}_2\text{O}_3$; this is equivalent to a solid solution of γ - Al_2O_3 . A small amount of mullite was also detected. The X-ray powder photograph of these compounds, together with the X-ray photographs of $\text{MgO}.\text{Al}_2\text{O}_3$, γ - Al_2O_3 , and α - Al_2O_3 for comparison with it, are given in Fig. 84. Spinel and alumina can be seen in the photo-

micrographs, the spinel predominating. The presence of this type of inclusion is one of the

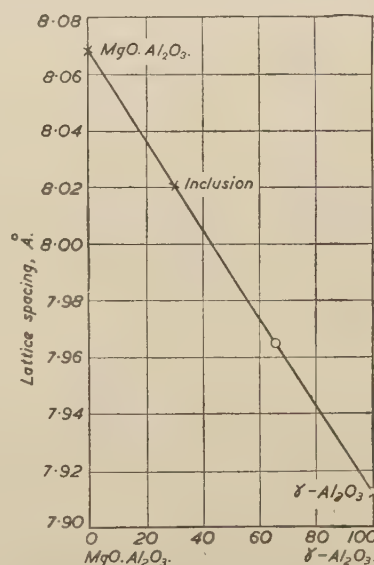


FIG. 90.—Lattice Spacing of Spinel observed in the inclusion (example 22), in relation to those of the $\text{MgO}.\text{Al}_2\text{O}_3$ - γ - Al_2O_3 system, assuming the validity of Vegard's law.

factors which always adversely affect machinability and drilling.

A similar result was found on investigating a carbon steel which also failed to drill freely. An X-ray photograph of the extracted powder is shown in Fig. 84(e).

Example 23.

Another example worthy of note was revealed during the examination of defects which had developed in a number of race rings made from imported basic open-hearth steel. Defects on the working surface were revealed only during final inspection and these defects took the form of what appeared to be random cracks. A typical inclusion is illustrated in Figs. 75, 76, and 77. Fig. 75 is a photograph ($\times 25$ dia.) and Figs. 76 and 77 are photomicrographs ($\times 500$ dia.) of the inclusion, unetched and etched with alkaline sodium picrate respectively. In the unetched specimen Al_2O_3 laths only could be identified but, after etching, further crystalline phases (one of which appeared to consist of mullite) were identified.

Such inclusions would be highly undesirable because, apart from initiating cracks under shock loading, they might work free and cause wearing of the bearings during service.

Example 24.

Prominent strings of what appeared to be alumina were found on a small gear-shaft (see Fig. 73); it was considered possible that confirmation of this might be obtained from the study of X-ray glancing-angle photographs. A discontinuous inclusion, 2 in. long, was therefore photographed by X-rays and compared with a photograph (obtained by identical means) of α -alumina. The two photographs can be seen in Fig. 85.

Although the structure of the two substances are identical, there is one significant difference in that the inclusion in the gear-shaft had a coarser grain-size, as indicated by the spotty nature of the α -alumina lines. There is no doubt that free alumina of this type was trapped in the steel, owing to the excessive oxidation of the added aluminium.

Example 25 (35% Cobalt Bar-Magnet Steel).

A magnet steel made by the electric crucible process was found to contain a prominent inclusion situated between the outside and centre of a bar. A section of the inclusion before etching was devoid of any indication of a crystalline structure. Etching in alkaline sodium picrate solution, however, revealed that the inclusion was partly crystalline (see Fig. 74). A portion was then removed mechanically for X-ray powder examination, after which the diopside type of structure

was identified. The relative intensities differed slightly from pure diopside ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$), approaching more nearly to augite, which is a monoclinic pyroxene, $\text{Ca}(\text{Mg}, \text{Fe})\text{O} \cdot 2\text{SiO}_2 \cdot (\text{Fe}, \text{Al})_2\text{O}_3$.

An X-ray photograph of this inclusion, showing the presence of these phases and their comparison with diopside and augite, is shown in Fig. 83.

Example 26.

A series of inclusions in two bath samples are the subject of the next example. Typical free-silica globules are apparent in the first bath sample (see Fig. 59). After addition of ferro-manganese they change in constitution, as shown in Fig. 60, so that the inclusion contains free silica in a silicate background, or consists entirely of silicate, as shown by the etched specimen (Fig. 72). This inclusion has the appearance of rhodonite, in the form of laths.

Classification of Non-Metallic Inclusions.

The non-metallic inclusions encountered in this investigation have been classified in Table XVII. The most probable sources of origin are indicated and the chief properties of the inclusions and methods of identification are outlined. It is not intended to convey that Table XVII. includes all types of non-metallic inclusions occurring in steel, but as it is a summary of the various types of inclusions found in a fairly exhaustive survey, it is concluded that these are the chief types generally found. Accordingly, consideration of Table XVII. should assist the steelmaker in detecting the sources of inclusions and in adopting preventive measures to avoid dirty steel. Attention has in the past been chiefly focused on the melting and deoxidation procedures, which were believed to be responsible for the most harmful non-metallic inclusions. Although the authors agree that careless melting and deoxidation can result in harmful non-metallics, there are other important sources of harmful inclusions (see Table XVII.) which have received little attention. It is not unusual for the melting and deoxidation technique to be carried out with all the care and attention likely to produce steel of satisfactory cleanness and quality and then to find that the steel is contaminated with large and harmful inclusions. This paper would be incomplete without suggesting means by which the results summarized in Table XVII. can be applied in practice.

PRACTICAL APPLICATIONS TO STEELMAKING.

Aluminous Inclusions.

Aluminium is commonly added to steel as a final deoxidant and grain-size controller. Analysis of aluminium-treated steel indicates that much of the aluminium has been oxidized to alumina.

TABLE XVII.—*Classification of the Most Frequently Occurring Non-Metallic Inclusions, Excluding Sulphides.*

Type of Inclusion.	Origin.		Identification.
	Basic-Electric Steel.	Acid Open-Hearth Steel.	
Aluminous α - Al_2O_3 $\text{MgO}.\text{Al}_2\text{O}_3$.	Oxidation of aluminium added for de-oxidation and grain-size control.		Characteristic appearance in polished section (<i>see</i> Figs. 51, 52, 64, 67, 68, 71, 76, and 77). Although spessartite may be mistaken for spinel, large amounts of α - Al_2O_3 are seldom associated with spessartite. Spinel and α - Al_2O_3 are strongly crystalline and, because of their high melting points, are not deformed during forging, rolling, &c.; frequently occur as "streaks," as distinct from stringers. Where a eutectic structure consisting of spinel and Al_2O_3 occurred, it was considered that some Fe or Mn was present in the spinel, lowering the fusion point. Inclusions extracted mechanically or by the Dickenson method can be identified with certainty by analysis, or by X-ray or microscopic examination.
Melilite (gehlenite)-rich.	Reaction product of tapping slag and aluminosilicate refractory (particularly ladle refractories).	Not detected.	Low melting points (about 1250–1300° C.), thus usually occur as stringers after forging, rolling, &c. Identification with certainty difficult in polished section although, occasionally, characteristic crystals occur (<i>see</i> Figs. 56 and 57). Dickenson extraction method unsatisfactory, as most of the CaO is lost, the constitution of the residue thus differing from that of the original inclusion. Mechanically removed inclusions may be identified by analysis, or X-ray or petrological examination.
Manganese aluminosilicates.	Corrosion of aluminosilicate, free-quartz-containing, refractories by the manganese of liquid steel (particularly tundish linings, in top casting, and uphill refractories, in uphill pouring). Ladle and launder refractories are also probable sources.		Low fusion points (1100–1200° C.), thus usually occur as stringers after clogging, &c. Presence of the Al_2O_3 -containing phases (manganese anorthite or spessartite) an almost certain criterion, particularly when aluminium has not been added. Cannot be identified with certainty in polished section (<i>see</i> Figs. 32 and 33), as are usually only partly crystalline and may be confused with ferrous manganous silicate deoxidation products; in such cases, crystallization may be developed by annealing. When microscopical identification is uncertain, the presence of Al_2O_3 in the Dickenson extract is a criterion when aluminium has not been added; X-ray examination a further method. Where mechanical extraction is possible, identification by means of analysis, X-ray, and petrological examination is simple. These compounds frequently occur as surface scums, underneath which small blow-holes are usually found; such scums are readily chipped out and identified.
Siliceous refractory	Erosion of siliceous refractory washes or cements of the ganister type. In top casting the chief source is probably the launder and ladle patching materials. In bottom pouring, ganister cement used in jointing the uphill refractories is an additional source.		Consist of primary crystals of tridymite or cristobalite embedded in a glassy matrix, Figs. 47 and 50 being typical examples. Apparently the small particles of siliceous refractories washed into the steel are fused tridymite or cristobalite, crystallizing from the glass on subsequent cooling. These inclusions may be confused with siliceous deoxidation products, but the "refractory" inclusions will contain combined Al_2O_3 , which, when crystallized, will be in the form of mullite. These inclusions, extracted mechanically or by the Dickenson method, may be identified by analysis, or X-ray or petrological examination.
Acid tapping-slag.		Slag trapped in the steel during pouring into ladle, or wash of slag layer from ladle lining.	Constitutions: (1) Primary crystals of tridymite or cristobalite associated with fayalite-tephroite solid solution or glass. (2) Primary crystals of silica associated with rhodonite or glass. (3) Primary crystals of rhodonite associated with silica or glass. (4) Vogtite associated with silica or glass. In acid steel, tapping-slag inclusions may have very similar microstructures to the previous type of inclusion, but the alumina content of the tapping-slag inclusions will be very much lower than that of the siliceous-refractory type.

TABLE XVII. (Continued).

Type of Inclusion.	Origin.	Identification.
Globular silica.	Probably product of deoxidation by silicon; more frequently found in acid steel.	These fused spheres of silica have a characteristic appearance (Fig. 59). Owing to their very high fusion-temperature they are not deformed during subsequent working of the steel.
Siliceous deoxidation products.	Products of deoxidation with silicomanganese or ferromanganese and ferro-silicon.	May have somewhat similar constitutions to the first three types of acid slag inclusions. Hence in acid steel, tapping-slag inclusions may be confused with deoxidation products, although the latter will tend to be smaller and more uniformly distributed.
Large refractory inclusions.	Usually pieces of firebrick and compo-ganister cement which have been eroded or spalled during passage of the steel over the casting refractories. Refractory materials may also spall from the compo- or firebrick-lined heat-boxes during teeming. Inadequate blowing-out of moulds is another cause of these inclusions, which are usually found near the surface of the ingot.	These large inclusions can be chipped out and easily identified by analysis or X-ray or microscopic examination.

Under ideal conditions, the alumina should occur as very small particles uniformly distributed throughout the steel. Frequently, however, large particles of alumina and spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$) occur as segregates and streaks. Owing to their extreme hardness, these inclusions are particularly obnoxious in easy-machining and drilling steels. Partial oxidation of aluminium cannot be prevented, because it is a stronger deoxidant than manganese or silicon, but its oxidation may be reduced to the minimum by adequate previous deoxidation of the steel by silicon. When aluminium oxidizes in the basic steel furnace, the resulting alumina tends to combine with the MgO of the dolomite hearth to form spinel. Accordingly, additions of aluminium to steel in the basic furnace should be avoided where possible and additions confined to the ladle. However, the causes of excessive oxidation of aluminium and segregation of the products of oxidation are not fully understood and require further detailed study.

Manganese Alumino-Silicates.

Manganese alumino-silicate inclusions, which are formed by the reaction of manganese in liquid steel with certain firebrick refractories, are plastic at the usual hot-working temperature of steel and elongate to form stringers, which adversely affect the transverse properties. It is suggested that these inclusions are a more frequent cause of failure of the steel to meet the required transverse properties than is generally realized. Uphill teeming is often practised when very clean ingot skins are required (such as for tyre steels), and when manganese alumino-silicates form they are often found on the skin as scums associated with blowholes and unsoundness.

McCance,⁴⁰ in discussing the manganese-silicon equilibrium in liquid steel, has claimed that the chemical reduction of silica in uphill-casting firebrick refractories by manganese could be suppressed by small additions of aluminium, thus considerably reducing the inclusions due to slagged refractory. However, the influence of the constitution of the firebrick was not taken into account, the assumption being made that all the silica present was attacked by the manganese, whereas Rait² has more recently shown that the constitution of the firebrick is extremely important, firebrick refractories free from quartz being attacked to a much lesser extent than those containing quartz. To reduce the formation of manganese alumino-silicates in uphill teeming to the minimum it is suggested that uphill-casting refractories free from quartz should be employed. In order to attain this desirable constitution, the firebricks should contain not less than 38% of Al_2O_3 ; slightly lower alumina contents may be found permissible, but less than 35% is inadvisable. When the refractories contain considerable amounts of quartz, the benefit of aluminium in suppressing the manganese reduction of silica is doubtful, because aluminium, being a stronger deoxidant than silicon, is oxidized by the SiO_2 to alumina; thus deleterious aluminous inclusions may be introduced.

The same considerations apply to all firebrick refractories, such as launders, ladle linings, stoppers and nozzles, tundishes, &c., with which the steel comes in contact after leaving the furnace. To reduce the formation of manganese alumino-silicates to the minimum, quartz should not be present in these refractories.

The corrosion of fireclay nozzles by the manganese of liquid steel to form manganese alumino-

silicates can be greatly reduced by boiling the nozzles in tar. The most probable explanation of this is that the free carbon deposited in the pores of the nozzle decreases the manganese reduction of silica—in accordance with Fig. 87—and the evaporation of the volatile fractions of the tar tends to produce a protective gaseous layer between the nozzle and the stream.

Melilite-Rich Inclusions.

Inclusions in which melilite is the most prominent constituent are produced by the fluxing action of basic-electric tapping slag on firebrick refractories. The amount of trapped-slag reaction product in the steel is probably reduced by preventing the slag from entering the ladle until it has received most of the steel. During teeming, however, the slag fluxes the ladle lining and some of this slagged surface will be washed into the following cast of steel. Hence it is extremely important that the slagged refractory should be cleaned as thoroughly as possible after each heat. The application of protective coatings of compo and ganister cements to ladle linings is of doubtful value, as, although the life of the lining is prolonged, the amount of refractory washed into the steel is probably increased.

The use of basic ladle linings should reduce the amount of gehlenite-rich inclusions, and incidentally the amount of manganese aluminosilicates, but satisfactory basic ladle refractories are not yet available and much further development work in this respect is required.

Siliceous Refractory Inclusions.

The patching of launders, ladles, and tundishes with plastic siliceous refractory cements is common practice. The majority of these materials have a weak cold-setting strength, and even with the drying temperatures normally employed they are fairly friable and easily eroded by the liquid steel. These patching materials are undoubtedly responsible for much of the siliceous type of inclusions found in steel and are also a source of manganese aluminosilicates. The development of basic refractory patching-cements having adequate setting strength at normal drying temperatures and resistance to erosion, is required.

Acid Tapping-Slag Inclusions.

Inclusions of this type seldom occur in steel. The fluxing action of acid slag on ladle linings is much less severe than that of basic slag, although a low-melting slag, consisting chiefly of pyroxene, is formed on the ladle lining. This low-melting product must be removed as thoroughly as possible, otherwise some of this slag will be washed into the following heat.

Siliceous Deoxidation Products.

Since much attention has been focused elsewhere on methods of deoxidation, further comment is not required.

Large Refractory Inclusions.

The majority of these inclusions can be avoided by careful pit practice. The spalling of the refractory lining of head-boxes may be avoided by the use of firebrick or compo with a high spalling-resistance index.

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THE NEUTRALIZATION OF SULPHUR IN CAST IRON BY VARIOUS ALLOYING ELEMENTS.*

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(Figs. 1 to 31 = Plates LIX. to LXIV.)

SYNOPSIS.

A metallographic examination has been made of the sulphide phases in irons of low manganese and high sulphur contents, to which varying amounts of nickel, molybdenum, copper, chromium, and aluminium have been added. In the absence of these elements, manganese and iron sulphides would have been present. Nickel in amounts up to 20% gave no new sulphides; molybdenum did not influence the form of the sulphides until 2% of the element had been added. In the presence of low manganese contents complex copper-sulphide/iron-sulphide/manganese-sulphide aggregates were obtained. Complex sulphides were found in all irons with chromium contents of between 1 and 30%; 2-7% of aluminium caused the sulphides to be present as an aluminium (manganese) sulphide. With sufficient manganese to balance normal sulphur contents, manganese sulphide was the only sulphide phase to be seen except in the case of high chromium contents.

Abnormal graphite structures were obtained in some of the irons containing nickel or copper. It is suggested that these are formed by the solidification of the iron in the white condition, followed by carbide breakdown after solidification. This process may be caused by the effect of temperature upon the reaction between manganese and iron sulphide.

INTRODUCTION.

IN a previous paper¹ the author has discussed the metallography of inclusions in cast irons of normal composition and in those containing titanium and zirconium. From this it is apparent that sulphur is an important alloying element in cast iron and, in addition to its direct carbide-stabilizing effects, has other major influences. It is largely unavoidable in cast iron with present raw materials and the existing manufacturing processes. Sulphur undoubtedly has undesirable features and this has led to its almost universal acceptance as an unavoidable evil and hence its amount is usually kept to a minimum. This principle has served and will continue to serve a useful function in general iron-foundry practice, but for the fuller development of the potentialities of cast iron it will be necessary to regard sulphur as a useful alloying element. In many respects sulphur as an alloying element is unique insofar as it can occur in many different forms as sulphides of other alloying elements, *e.g.*, manganese, titanium, zirconium, vanadium, copper, chromium, aluminium, &c. The effect of sulphur in cast iron depends almost entirely upon the manner in which it is combined with another element, that is, upon which sulphide is formed.

The elements nickel, molybdenum, copper, chromium, and aluminium, all form fairly stable sulphides, and it was the object of the work here reported to determine to what extent each of these elements could combine with sulphur in cast iron. In most commercial cast irons sulphur exists as manganese sulphide. Routine examination over a number of years of samples containing sulphur in this form showed that nickel in amounts up to about 20% had little or no effect on the mode of occurrence of the manganese sulphide; copper, on the other hand, had little effect in amounts up to about 2.0%; beyond this the manganese sulphide developed a marked blue coloration increasing in intensity with increasing amounts of copper until, when free primary copper was present, the sulphide tended to segregate in the copper globules. Chromium also had little effect on manganese sulphide in amounts up to 2%, but in heat-resisting irons containing 30% of chromium the manganese sulphide was replaced by another sulphide. Molybdenum did not appear to have any effect in amounts up to 1.5% on the manganese sulphide; aluminium had little effect in amounts up to 8%.

It was obvious from these preliminary observations that the predominating affinity of manganese for sulphur largely prevented the combination of

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these alloying elements with the sulphur, except in the case of very high copper and chromium contents. Therefore, in order to investigate the possibility of the occurrence of the sulphides of these elements it was necessary to work with a low manganese content and a high sulphur content so that free iron sulphide would be present in the microstructure. Under these conditions sulphur exerts a marked carbide-stabilizing effect. The elements nickel, copper, and aluminium, are graphitizing elements, and when added to such a base iron they might exercise a graphitizing effect *per se*, and also by neutralizing the effect of the sulphur by forming other sulphides with it. A base iron with a relatively low manganese content (pig iron A) was therefore chosen for this investigation; in addition, some experiments were carried out with a Swedish white iron (pig iron S). The compositions of these two irons were as follows :

	Pig Iron A.	Pig Iron S.
Total carbon, %	3.93	4.0
Silicon, %	0.88	0.2
Manganese, %	0.30	0.10
Sulphur, %	0.145	0.005
Phosphorus, %	0.03	0.04

MELTING PROCEDURE AND SUBSEQUENT TESTS.

A charge of base iron and steel scrap, together with the necessary amount of alloy, was melted in a coke-fired, forced-draught furnace (except in the case of aluminium when the aluminium was added after the charge had melted). When molten, the melt was treated with a weighed amount of iron sulphide and from the larger melts four 1.2-in. dia. test-bars were top-poured at successively lower pouring temperatures into green-sand moulds. In the case of melts of the Swedish white iron, the charges were smaller and only one test-bar was poured. In the copper series an additional group of melts was carried out to cast 3-in. dia. bars, and some small ingots were cast from a high-frequency induction-furnace melt. Particulars of the latter melt were as follows : The initial charge consisted of 1600 g. of Swedish wrought iron and 96 g. of electrode carbon. When the iron was molten 17.6 g. of iron sulphide and 12 g. of copper were added and an ingot 0.875 in. in dia. (1F3) was cast. Another 9.75 g. of copper were added to the melt and ingot 1F4 was poured. This process was repeated for additions of 15 g. and 21 g. of copper, ingots 1F5 and 1F6 being cast after each, respectively. Each ingot weighed approximately 300 g.

The addition of iron sulphide to the melt caused, in most cases, a marked turbulence with the evolution of considerable quantities of gas. This caused the majority of the test-bars to show extensive unsoundness and so the results of the

mechanical tests were of little value and have not been reproduced here.

After breaking in transverse, a micro-specimen was taken at the fractured end of each bar. The samples for chemical analysis were taken adjacent to the spot used for micro-examination.

In addition to the melts containing alloys, a melt was carried out with the iron sulphide addition alone. This showed no unusual features, having a structure of a typical hypo-eutectic white iron with considerable amounts of manganese and iron sulphide.

All the micrographs reproduced in this paper at 1500 diameters were taken with a 2-mm. oil-immersion achromat *N.A.* 1.3. Those at 800 diameters were taken with a 4-mm. dry apochromat *N.A.* 0.95, and those at 60 diameters were taken with a 16-mm. achromat *N.A.* 0.28, using no eyepiece. A yellow filter was used in every case. The micrograph in Fig. 20 was taken with a 1.8-mm. mono-bromo-naphthalene immersion objective *N.A.* 1.6, using a deep-blue filter.

EXPERIMENTS WITH THE VARIOUS ELEMENTS AND THE RESULTS OF MICROSCOPIC EXAMINATION.

The Nickel Series.

There are very few references in the literature to the possibility of a nickel sulphide occurring in ferrous alloys. The nickel-sulphur system has been studied and a useful summary of this work is given by Hansen.² Merica and Waltenberg³ report the occurrence of nickel sulphide (Ni_3S_2) as a yellow phase in nickel containing more than 0.005% of sulphur. This sulphide has a freezing point at approximately 790° C. Vogel and Tonn⁴ have investigated the iron-nickel-sulphur system and in the iron-rich corner of the equilibrium diagram they indicate iron sulphide (FeS) to be the only sulphide phase present. Nickel sulphide only occurs in this system with very high concentrations of nickel and sulphur which are completely outside the range likely to be found in cast irons. It would appear from the information available in the literature that nickel would not be expected to form a sulphide in cast iron.

Nine melts were carried out in this series and the microstructures and chemical analyses are given in Table I.

In all cases the only sulphides present were iron sulphide (which almost certainly contains manganese sulphide in solution) and manganese sulphide (which contains iron sulphide in solution). This confirms the indications given in the literature and as a result of these experiments it is felt that it may be safely stated that nickel in amounts up to about 20% in cast iron does not affect the form in which the sulphur exists.

As far as the effect of nickel on the matrix

structure was concerned, the structures obtained were quite normal and are indicated in Table I.

Samples *MS/499*, *MS/500*, *MS/525*, and *MS/524*, had typical hypo-eutectic white-iron structures, but in *MS/520* an abnormal graphite structure appeared. This iron was mottled but did not contain normal graphite flakes. Instead, the graphite was distributed around the lakes of cementite in the mottled regions in a mesh-like pattern. A typical spot taken from specimen *MS/520* is illustrated in Fig. 1. This structure has been reported previously¹ in an iron containing titanium and vanadium which had been treated with iron sulphide. In addition to these graphite formations a few spherulitic carbon nodules of a very small order of size were noted (Fig. 2). In the case where this mesh-like

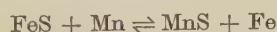
reaction tends to proceed to the left, that is, to give increasing amounts of iron sulphide and, conversely, as a casting cools, the amount of manganese sulphide should increase. It is also a well-established fact that sulphur in the form of iron sulphide exerts a pronounced carbide-stabilizing effect, and when in the form of manganese sulphide it behaves neutrally. Thus at certain critical compositions it is conceivable that during solidification sufficient sulphur may be present as iron sulphide to effect carbide stabilization, but at some temperature shortly after solidification, when more manganese sulphide has formed and less iron sulphide is present, there will be less of this latter phase to maintain a stable carbide (under these conditions of cooling) and graphitization will occur.

TABLE I.—*Microstructures and Analyses of Samples in the Nickel Series.*

Sample.	Pig Iron.	Microstructure.	Analysis.				
			T.C. %.	Si. %.	Mn. %.	S. %.	Ni. %.
<i>MS/499</i>	<i>A</i>	Pearlite + cementite	2.87	0.76	0.25	0.526	0.88
<i>MS/500</i>	<i>A</i>	Pearlite + cementite	3.22	0.80	0.18	0.466	1.77
<i>MS/520</i>	<i>A</i>	Very fine pearlite + cementite and graphite	2.89	0.85	0.20	0.497	3.13
<i>MS/519</i>	<i>A</i>	Martensite in austenite + graphite and cementite	2.50	1.02	0.20	0.494	6.79
<i>MS/544</i>	<i>A</i>	Austenite + graphite	2.89	1.47	0.25	0.509	13.68
<i>MS/545</i>	<i>A</i>	Austenite + graphite	2.88	1.73	0.20	0.609	20.19
<i>MS/525</i>	<i>S</i>	Pearlite + cementite	3.04	0.21	0.15	0.308	1.73
<i>MS/524</i>	<i>S</i>	Very fine pearlite + cementite	2.90	0.32	0.19	0.285	3.28
<i>MS/523</i>	<i>S</i>	Martensite in austenite + graphite and cementite	2.84	0.45	0.15	0.304	6.31

graphite structure was noted previously it was suggested that it formed by decomposition of cementite after solidification. Its occurrence in this series containing nickel in no way disproves the theory, and, in the author's view, the simultaneous occurrence of spherulitic carbon nodules adds further support to the idea. It is of interest to consider by what mechanism irons of this composition tend to give this structure.

In cast irons and steels the reaction between manganese and iron sulphide may be represented by the equation :



The reversibility of this reaction is well established and for all the sulphur to be present as manganese sulphide it is necessary to have an excess of manganese over the theoretical percentage indicated by the formula (MnS). The irons prepared for this work had relatively low manganese and high sulphur contents, and as a result, the reaction never proceeded to completion with these concentrations; and so there resulted an equilibrium mixture of manganese sulphide and iron sulphide (and manganese). At higher temperatures the above

Sample *MS/524*, made from the Swedish iron and having a nickel content close to that of *MS/520* but with a lower sulphur content and a very much lower silicon content, was completely white. No doubt the low silicon content was the predominating factor. Sample *MS/519* was similar to *MS/524* but, as one would expect with the higher nickel content, it contained much more graphite and much less cementite. Sample *MS/523*, made from the Swedish iron and with a nickel content similar to that of sample *MS/519* but with lower silicon and sulphur contents, closely resembled *MS/519*, showing well-developed mesh-like graphite clearly delineating areas of eutectic carbide, but rather more and better-developed graphite spherulites.

The two remaining samples, *MS/544* and *MS/545*, containing 13.7% and 20.2% of nickel respectively, were completely grey, and at low magnifications the graphite appeared to be of the well-known supercooled variety in a characteristic interdendritic distribution. However, at high magnifications the graphite was obviously not supercooled but mesh-like graphite; no individual graphite flakes were visible and all the graphite was

in the form of a reticulated membrane. In these cases the graphitizing effect of nickel was sufficient to cause complete graphitization after solidification if the theory given above is correct. A typical illustration of these graphite structures is given in Fig. 15. Although this micrograph was taken from an iron in the copper series (described later) the two structures are adequately illustrated by this one micrograph.

It is not suggested that these structures are the result of a unique effect of nickel in the presence of a high sulphur content. They have been produced to some extent previously in an iron containing no nickel and, as will be shown later, they have occurred in samples containing copper.

The Molybdenum Series.

No evidence was found in the literature indicating the interaction of molybdenum and sulphur in steels or cast irons, and no information was available on the molybdenum-sulphur system.

TABLE II.—*Microstructures and Analyses of Samples in the Molybdenum Series.*

(Pig iron A used in each case.)

Sample.	Microstructure.	Analysis.				
		T.C, %.	Si, %.	Mn, %.	S, %	Mo, %.
MS/517	Cementite + pearlite	3.04	0.76	0.29	0.498	0.54
MS/518	Cementite + pearlite	2.84	0.67	0.24	0.494	0.96
MS/556	Cementite + pearlite	3.11	0.79	0.29	0.488	1.50
MS/557	Cementite + pearlite + trace of acicular structure	3.08	0.91	0.28	0.514	1.87
MS/558	Cementite + acicular structure	2.92	0.93	0.25	0.544	2.00

By heating molybdenum wire in an atmosphere of sulphur vapour at 1100° C. for 1 hr., a thin coating of molybdenite (molybdenum sulphide (MoS_2)) was obtained. By the addition of sulphur to molten ferro-molybdenum a dull grey phase was obtained embedded in the metallic matrix. This may have been an iron-molybdenum sulphide.

To investigate the effect of molybdenum in high-sulphur cast irons, five melts were carried out. The ferro-molybdenum (67.8% of molybdenum) alloy addition was placed in the cold crucible along with the rest of the charge and as a result considerable losses of molybdenum were experienced.

The microstructures obtained and the chemical analyses are given in Table II.

As far as the general microstructure of these irons is concerned, at low magnifications they are all typical hypo-eutectic white irons. MS/517, MS/518, and MS/556, all show primary dendrites transformed to pearlite, but MS/557 shows very coarsely laminated pearlite with traces of the acicular structure. In these four irons the sulphides present are the normal manganese sulphide

and iron sulphide phases; the molybdenum did not appear to influence the mode of occurrence of the sulphur. In sample MS/558 (containing 2% of molybdenum), however, at high magnifications a group of new phases occurred; the primary dendrites were entirely transformed to an acicular structure. Considerable quantities of normal manganese-sulphide/iron-sulphide duplex particles were present and in some areas of the eutectic carbide a complex structure was visible. This structure was on a very fine scale, but appeared to consist of cementite as the continuous phase with finely divided particles of ferrite, a hard white constituent standing up in relief from the cementite, and a grey-khaki phase. The hard white phase was similar to that observed as the fourth phase in the phosphide eutectic of an iron containing molybdenum,⁵ and it is tentatively suggested that this is a molybdenum carbide. The grey-khaki phase strongly resembled iron sulphide except for its marked greyish appearance.

Under polarized light between crossed nicols it exhibited a faint anisotropy. By etching tests it could not be differentiated from iron sulphide. It is suggested that the phase is iron sulphide combined with molybdenum. Fig. 3 illustrates a typical aggregate of manganese sulphide and iron sulphide in this sample. Fig. 4 shows an area of "eutectic" carbide with no further phases in it, and Fig. 5 shows a carbide area with fine spots of ferrite, "molybdenum carbide," and the sulphide phase.

The Copper Series.

No information was discovered in the literature which had any direct bearing on this investigation upon the effect of copper on the mode of occurrence of sulphur in cast iron or steels. In irons containing sufficient manganese to balance the sulphur content as manganese sulphide, copper does not appear to have any obvious influence, but in such irons also with sufficient copper to give primary globules, the manganese sulphide tends to segregate in the massive free-copper areas. This has been illustrated previously by Nicol

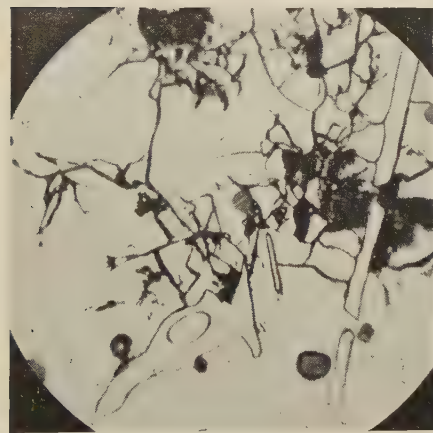


FIG. 1.—Sample MS/520, showing graphite arranged round lakes of eutectic cementite. Unetched. $\times 1500$.



FIG. 2.—Sample MS/520, showing occurrence of small graphite spherulites. Unetched. $\times 1500$.

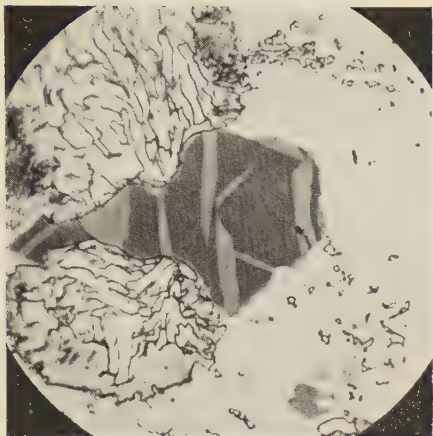


FIG. 3.—Sample MS/558, showing a typical MnS FeS aggregate. $\times 1500$.

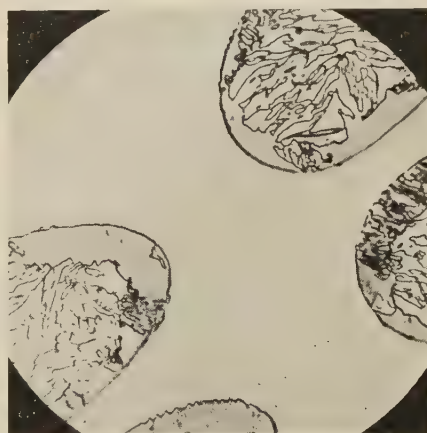


FIG. 4.—Sample MS/558, showing a typical area with carbide entirely free from structural complications and other phase. $\times 1500$.

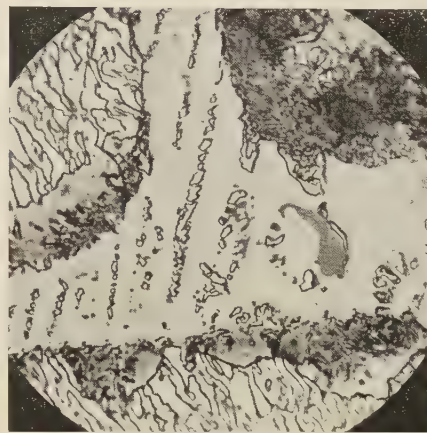


FIG. 5.—Sample MS/558, showing sulphide associated with a complex structure in cementite. $\times 1500$.

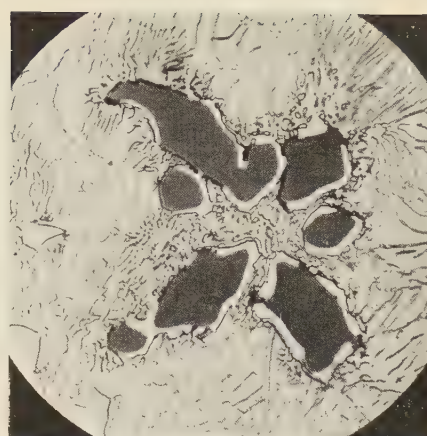


FIG. 6.—Sample MS/574, showing manganese sulphide surrounded by carbide. $\times 1500$.

Figs. 3 to 6 Etched with Picric Acid.
(Micrographs reduced to four-fifths linear in reproduction.)

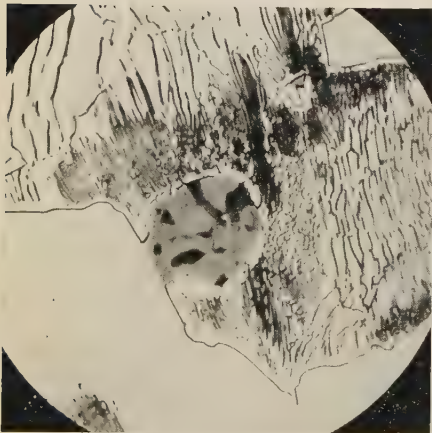


FIG. 7.—Sample MS/574, showing iron sulphide containing deep brown phase. $\times 1500$.

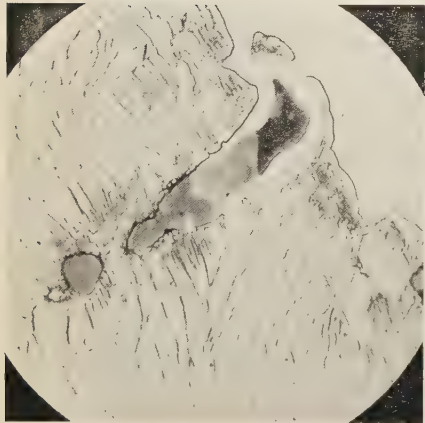


FIG. 8.—Sample MS/574, showing a complex aggregate of MnS, FeS, and the deep brown phase. $\times 1500$.

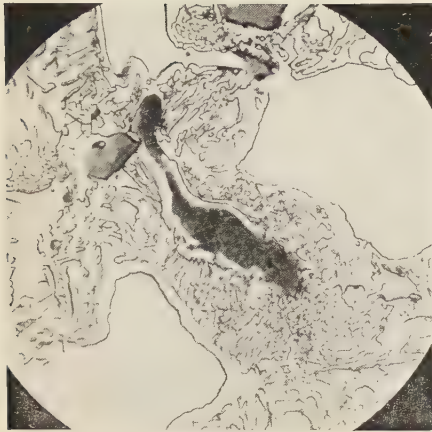


FIG. 9.—Sample MS/575, showing a eutectic-like particle. $\times 1500$.

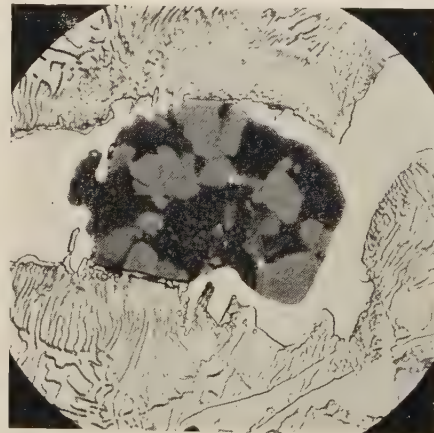


FIG. 10.—Sample MS/576, showing a typical aggregate of manganese sulphide and the deep brown phase.

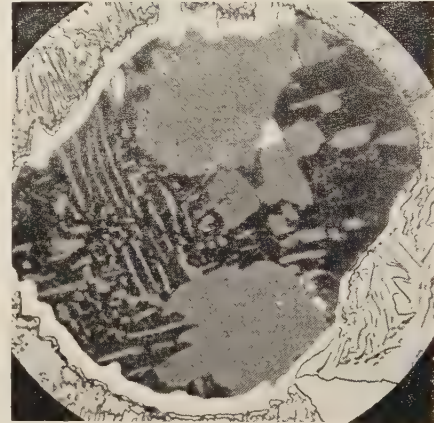


FIG. 11.—Sample MS/576, showing an aggregate of MnS crystals, MnS lamellae, and the deep brown phase. $\times 1500$.

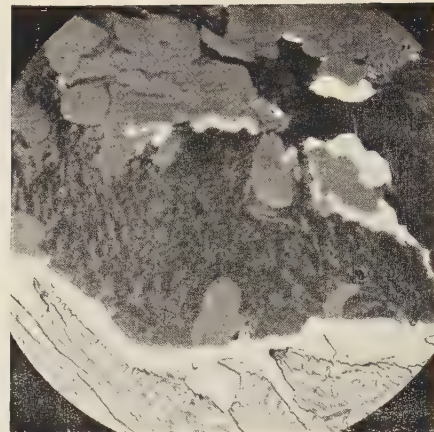


FIG. 12.—Sample MS/578, showing crystals of MnS in a eutectic-like matrix at the edge of a large sulphide blob. $\times 1500$.

All etched with picric acid.

(Micrographs reduced to four-fifths linear in reproduction.)

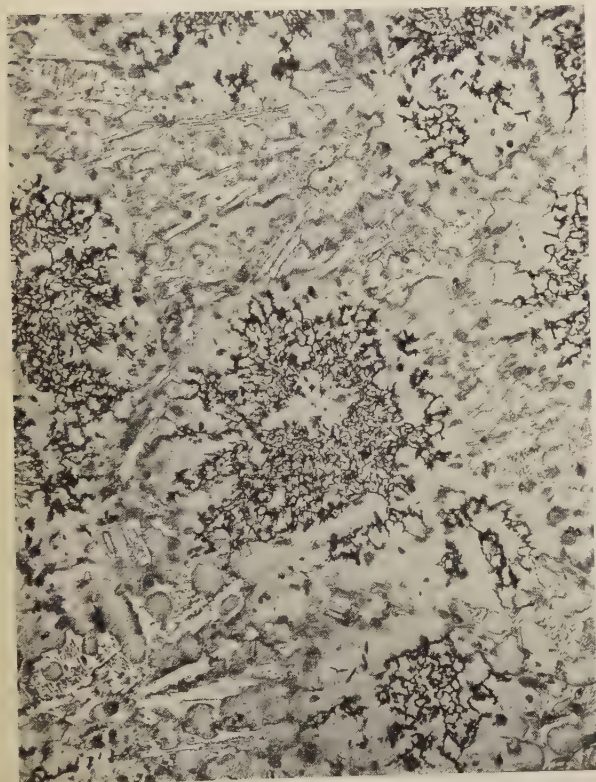


FIG. 13.—Sample MS/580, 0.63% of copper.
FIGS. 13 and 14.—The General Structure of 3-in. Dia. Bar with different copper contents. Etched with picric acid. $\times 60$.

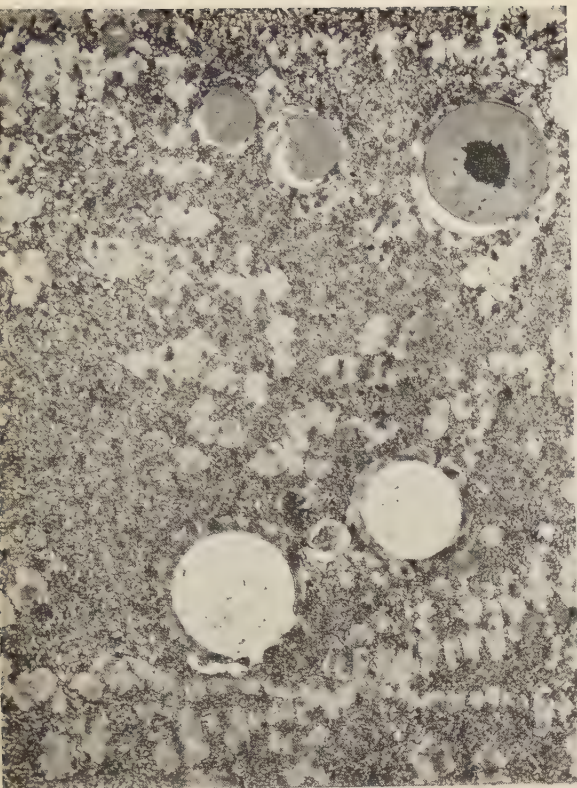


FIG. 14.—Sample MS/583, 5.26% of copper.
FIGS. 13 and 14.—The General Structure of 3-in. Dia. Bar with different copper contents. Etched with picric acid. $\times 60$.

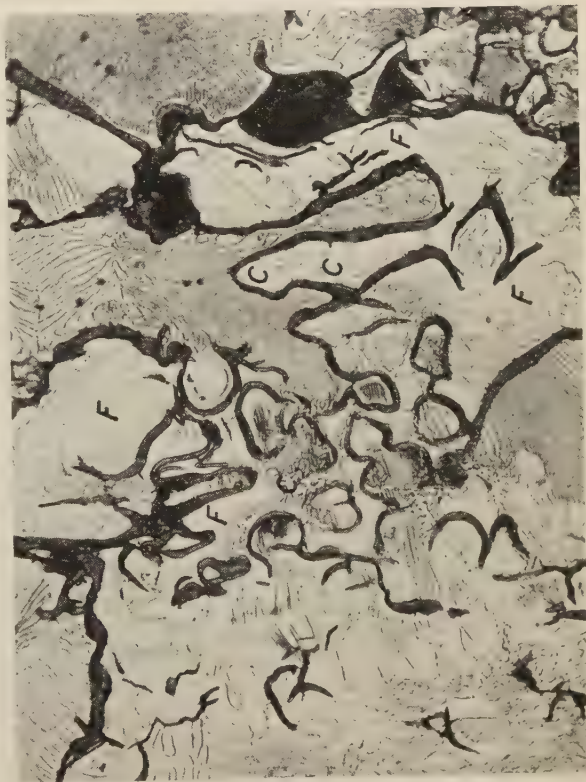


FIG. 15.—Graphite Formations Outlining Pre-Existing Cementite.

FIGS. 15 and 16.—Sample MS/583, showing graphite formations near the edge of 3-in. Dia. Bar. C cementite areas, F ferrite areas.

Both specimens etched with picric acid. $\times 800$.
(Micrographs reduced to four-fifths linear in reproduction.)

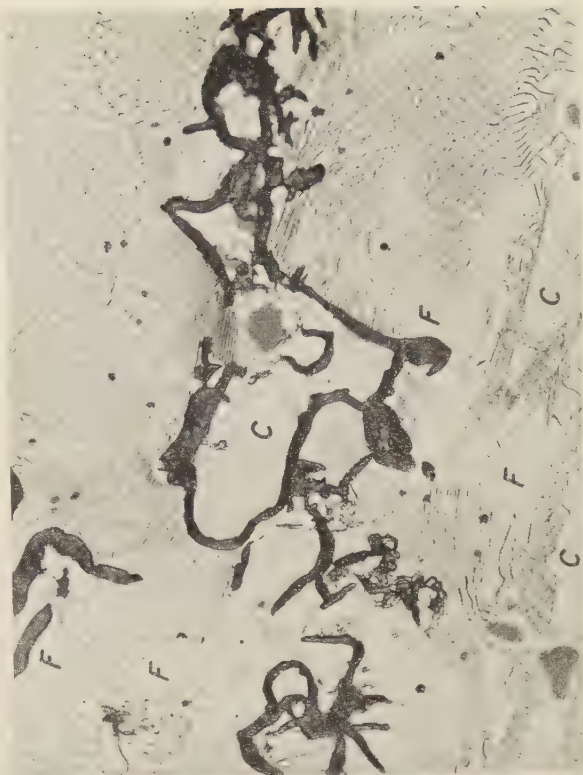


FIG. 16.—Graphite Formations Tending to Outline Pre-Existing Cementite.

Both specimens etched with picric acid. $\times 800$.
(Micrographs reduced to four-fifths linear in reproduction.)

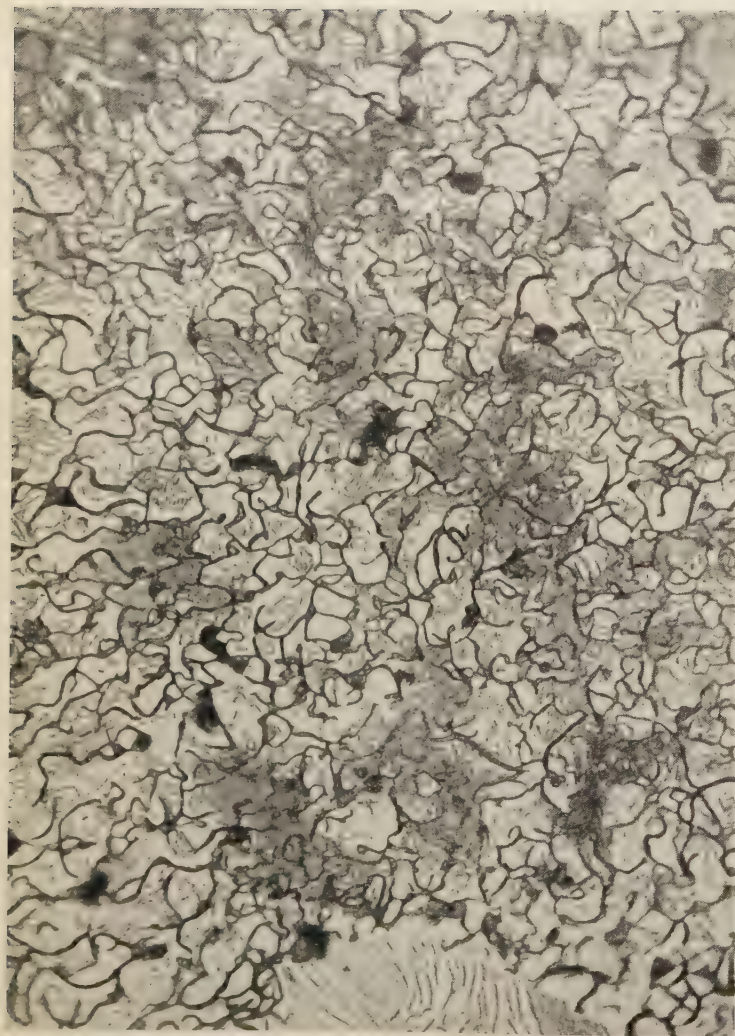


FIG. 17.—Sample MS/583, showing mesh-like graphite in structure of 3-in. Dia. Bar. Etched with picric acid. $\times 800$.

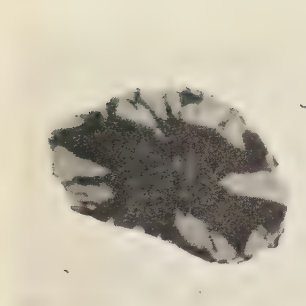


FIG. 20.—Complex Sulphide Particles in a Chilled-Roll Sample with 0.35% Mn, 0.085% S, and 1.03% Cr. Etched with picric acid. $\times 1250$.

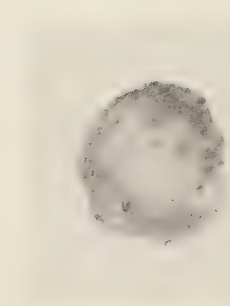


FIG. 21.—Sample MS 587, showing sulphide as dark green spheroid. Unetched. $\times 1500$.

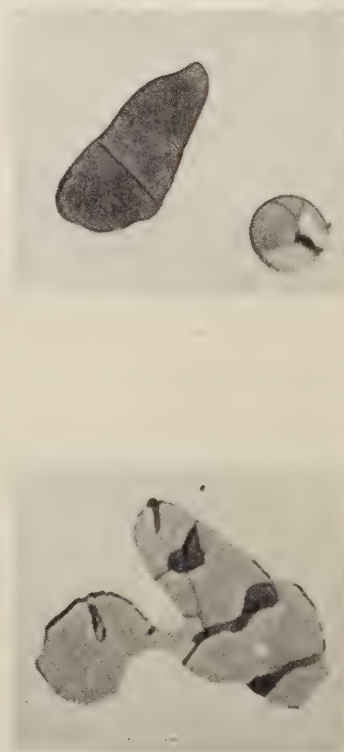


FIG. 18.—Sample IF4.

FIGS. 18 and 19.—Ferrous Sulphide Aggregates with a Deep Brown Phase. Unetched. $\times 1500$.



FIG. 22.—As Fig. 30, but between crossed nicols.

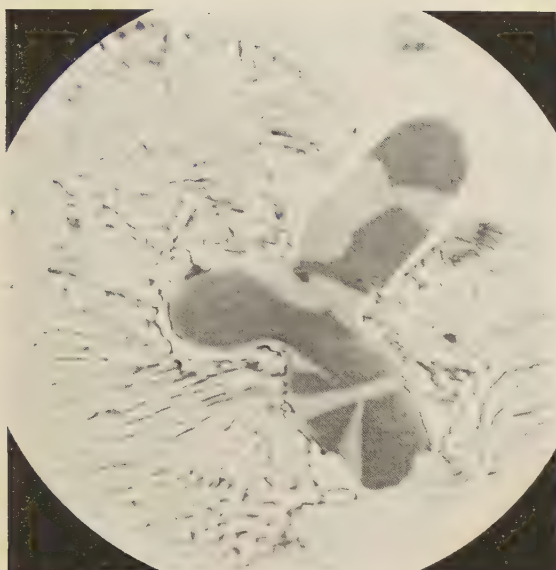


FIG. 23.—Sample *MS/566*.

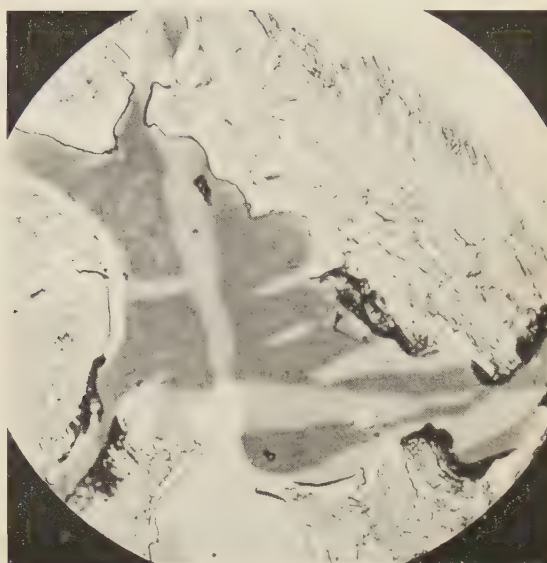


FIG. 24.—Sample *MS/568*.

FIGS. 23 and 24.—Typical Sulphide Aggregates, showing striations in the FeS. Etched with picric acid. $\times 1500$.



FIG. 25.—Sample *MS/570*, showing pronounced striations in a FeS-CrS Particle. Etched with picric acid. $\times 1500$.

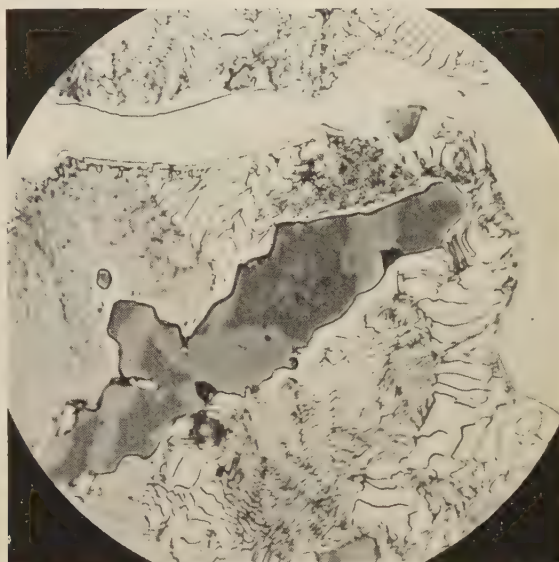


FIG. 26.—Sample *MS/570*, showing spotted structure in the MnS. Etched with picric acid. $\times 1500$.

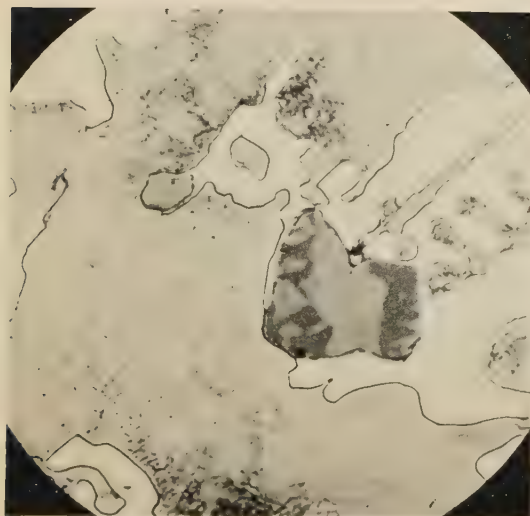


FIG. 27.—Sample MS/617.

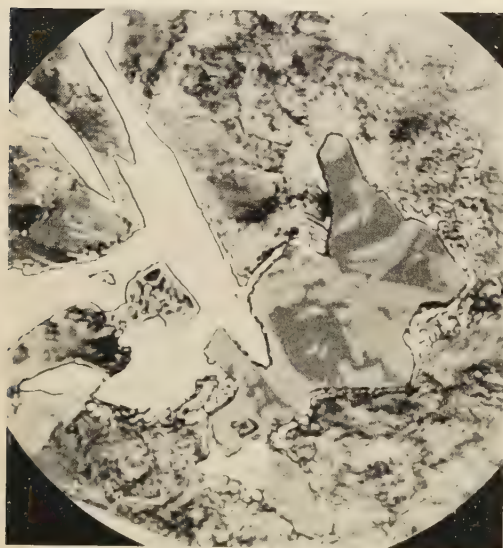


FIG. 28.—Sample MS/618.

Figs. 27-29.—Typical Sulphide Aggregates. Etched with picric acid. $\times 1500$.

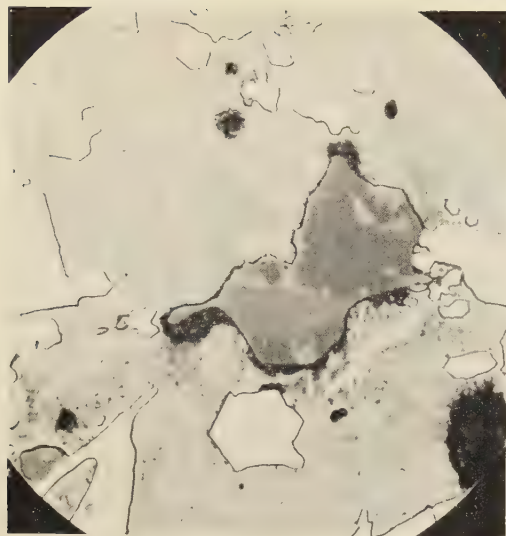


FIG. 29.—Sample MS 625.

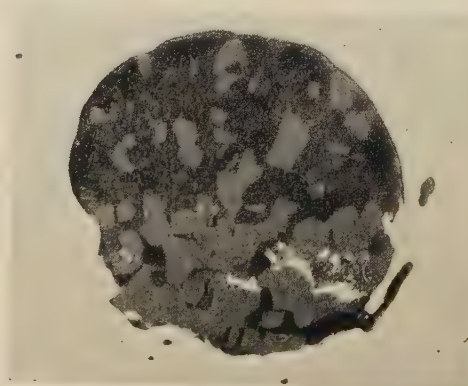


FIG. 30.—Sample MS/157, showing sulphide sphere. Unetched. $\times 1500$.

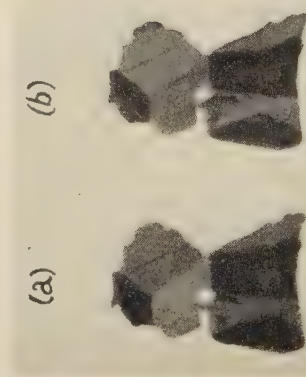


FIG. 31.—Sample MS/591, showing (a) a typical sulphide aggregate, and (b) the same group as (a) but after rotating the specimen through 90° . Unetched. $\times 1500$.



FIG. 32.—As Fig. A, after 10 min. in 10% chromic acid at 18°C . $\times 135$. (See J. H. Whiteley's contribution.)

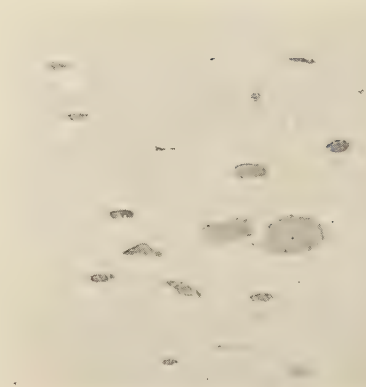


FIG. A.—Sulphide Inclusions in a 0.45% Sulphur Steel. $\times 135$. (See J. H. Whiteley's contribution.)

Smith.⁶ Norbury and Morgan⁷ have found that the occurrence of primary globules of free copper tends to promote the formation of supercooled graphite and they have attributed this effect to the fact that copper in excess of the liquid solubility would coat the solid inclusions with liquid and render them non-inoculating. It would appear from these observations that manganese has a greater affinity for sulphur than has copper, which confirms the opinion of Schütz.⁸ However, the present investigator has observed that the manganese sulphide entrapped in primary copper globules frequently has a marked blue coloration, particularly when the manganese content is only just sufficient to balance the sulphur.

The copper-sulphur system has been investigated⁹ and shown to have a eutectic point at approximately 0.77% of sulphur and at 1067° C., the eutectic consisting of copper and cuprous sulphide (Cu_2S). Cuprous sulphide has a melting

deep brown phase (Fig. 7). Frequently all three occurred together in the same particles and occasionally the deep brown phase had a very fine eutectic-like structure with itself as the continuous phase and a light blue dispersed phase in the form of very small round spots. Fig. 8 illustrates one such complex particle with manganese sulphide at the top, iron sulphide at the centre, and the deep brown phase with eutectic-like blue spots at the bottom. This eutectic-like structure was very fine and only just visible on the original micrograph. It was found that etching in dilute aqueous ammonium salts caused the deep brown phase to assume a bright blue-purple coloration and the same effect was obtained by polishing the specimen with alumina prepared from ammonium alum. By polishing with carefully washed alumina prepared from aluminium sulphate, or by polishing with magnesium oxide, what is assumed to be the normal brown coloration was obtained.

TABLE III.—*Microstructures and Analyses of Samples in the Copper Series.*

Sample.	Pig Iron.	Microstructure.	Bar. Dia. in.	Analysis.				
				T.C. %.	Si. %.	Mn. %.	S. %.	Cu. %.
MS/574	A	Cementite + pearlite	1.2	2.93	0.72	0.24	0.473	0.81
MS/575	A	Cementite + pearlite	1.2	2.83	0.74	0.24	0.531	1.47
MS/576	A	Cementite + pearlite	1.2	3.03	0.75	0.21	0.346	2.94
MS/578	A	Cementite + pearlite	1.2	2.78	0.63	0.15	0.309	5.37
MS/580	A	Pearlite + cementite + graphite	3	3.27	0.87	0.12	0.312	0.63
MS/581	A	Pearlite + graphite + cementite	3	3.27	0.87	0.14	0.337	1.79
MS/582	A	Pearlite + graphite + cementite	3	3.33	0.94	0.08	0.232	2.57
MS/583	A	Pearlite + graphite	3	3.69	0.85	0.12	0.270	5.26
MS/156	S	Cementite + pearlite	1.2	0.13	0.275	1.65
MS/149	S	Cementite + pearlite	1.2	0.10	0.222	3.29
MS/157	S	Cementite + pearlite	1.2	0.11	0.200	5.88

point of 1127° C. and according to von Schwarz¹⁰ has a blue-grey appearance. The cuprous-sulphide/ferrous-sulphide system has been investigated but the claims made in the literature are somewhat confusing. Röntgen¹¹ obtained a liquidus curve with maximum points corresponding to the double sulphides $\text{Cu}_2\text{S} : \text{FeS} = 3 : 2$, $\text{Cu}_2\text{S} : \text{FeS} = 1 : 1$, and $\text{Cu}_2\text{S} : \text{FeS} = 2 : 5$, whilst Hofman¹² found a simple eutectiferous system.

Eleven melts were carried out in this series and the microstructures and the chemical analyses are indicated in Table III.

The first four melts were carried out according to the standard procedure described previously and these will be dealt with first.

Sample MS/574, containing 0.81% of copper, showed at least three different sulphide phases. First, normal manganese sulphide crystals were present in fairly large amounts and were generally surrounded by a thin film of carbide (Fig. 6). Iron sulphide was present, and usually associated with a

The production of this blue-purple film by ammonium salts is taken to indicate the presence of copper in the deep brown phase and it is suggested that it is either a solid solution of Cu_2S in FeS or a double sulphide, the stoichiometrical ratio being unknown. The light blue dispersed phase in the deep brown phase may be Cu_2S , MnS , or a double sulphide of these two.

Sample MS/575, containing 1.47% of copper, was similar to the previous sample, but the fine eutectic-like structure in the deep brown phase tended to be more clearly developed in most cases. A typical example of this is shown in Fig. 9.

Sample MS/576, containing 2.94% of copper, was similar to the previous sample but it had much less iron sulphide. Manganese sulphide and the deep brown phase with the eutectic-like appearance occurred together in round blobs. A typical spot is illustrated in Fig. 10. One abnormal case was noted where the blob contained manganese sulphide crystals and manganese sulphide lamellae

in a background of the deep brown phase with the fine blue spot; this is shown in Fig. 11. Great difficulty was experienced in resolving and photographing the eutectic-like structure. Whilst all the specimens illustrated here clearly showed the duplex character of the structure when examined visually, the actual pattern may not be clearly apparent on the micrographs. Visually, the structure was easily resolved with a monobromo-naphthalene immersion objective *N.A.* 1.6, but using the deep blue filter necessary with this lens all photographic contrast was lost.

Sample *MS/578* (5.37% of copper) contained no free iron sulphide but only large round blobs with a structure showing crystals of manganese sulphide in a matrix of the fine eutectic-like structure previously described. A typical example of the structure of such an aggregate is illustrated in Fig. 12. Here the eutectic-like structure is relatively coarse, and the light areas in the interior of the aggregate are free copper, which is to be expected at this composition.

Apart from the sulphides, all the bars referred to so far had a typical hypo-eutectic white-iron structure. Samples *MS/156*, *MS/149*, and *MS/157*, which were prepared from Swedish white iron, were all very similar to those prepared from pig iron *A* with similar copper contents. As an example, Fig. 30 shows a sulphide aggregate in sample *MS/157* (5.88% of copper). Crystals of manganese sulphide are seen together with a small amount of free copper and the fine eutectic-like structure. Again, these three samples had typical hypo-eutectic white-iron structures.

Generally copper is assumed to have a graphitizing action not differing greatly from that of nickel, and experience with normal compositions confirms this view. In the present case, however, it will be noted that whilst graphite began to appear with 3.1–3.3% of nickel and was present in a fair quantity with over 6%, no graphite was present even with nearly 6% of copper. In order to investigate the type of graphite likely to be formed in the presence of high sulphur contents and copper, four further melts were carried out and a 3-in. dia. bar, approximately 20 in. long, was cast from each melt. It was further thought that the accompanying slower cooling rate would give coarser sulphide particles and so permit a closer scrutiny of the eutectic-like structures. Details of the microstructures and the chemical analyses are given in Table III. These bars were broken in transverse and all the fractures were sound; the results are given in Table IV.

The sulphide aggregates in these large test-bars were on a very coarse scale and for the most part were exactly similar to those in the smaller bars cast previously. Significantly, the eutectic-like structure of the deep brown continuous phase and

the light blue dispersed phase was not appreciably coarser. If this is a eutectic structure it would be expected to be sensitive to changes in cooling rate and to give an increased particle size. In most cases in this series the manganese sulphide appeared to be cored. The interior of the crystals had a typical dove-grey colour but at the extremities they gradually changed until they appeared bright blue. It is suggested that this indicates a gradual increase in copper content of the manganese sulphide during its formation and, taken together with the observations made in the preliminary remarks, points to some intersolubility of Cu_2S and MnS . It was not found possible to photograph this coring effect in monochrome.

TABLE IV.—*Results of Transverse Tests on 3-in. Dia. Test-Bars.*

Sample.	Transverse Rupture Stress, tons/sq. in.	Fracture.
<i>MS/580</i>	29.2	Mottled.
<i>MS/581</i>	31.3	Mottled.
<i>MS/582</i>	25.6	Fine grey with white network.
<i>MS/583</i>	28.4	Fine grey.

The graphite structures of these bars showed several interesting features. Fig. 13 illustrates the general structure of sample *MS/580* containing 0.63% of copper. Clusters of graphite are seen with a network of eutectic cementite, the matrix being coarse pearlite. Detailed examination shows that the graphite is not normal and possesses some of the characteristics of mesh-like graphite described previously, insofar as the graphite flakes all tend to be joined together in any one cluster. Samples *MS/581* and *MS/582*, having 1.79 and 2.57% of copper, respectively, show similar structures but increasing copper gives decreasing amounts of carbide until *MS/582* contains only a very small amount. Sample *MS/583*, containing 5.26% of copper, is completely grey with mesh-like graphite in a matrix of pearlite. Fig. 14 shows the general structure of this bar. As in Fig. 13, the mesh-like graphite is in a pearlite matrix; the light globules are free copper and the darker ones are sulphide aggregates. The manner in which the mesh-like graphite is connected in one continuous membrane is shown in Fig. 17 at a higher magnification. It will be noted that all the graphite is connected and it is exactly similar in form to that which occurred in the nickel series.

At the edge of this bar a band about $\frac{1}{10}$ in. deep occurred in which the graphite was on a much coarser scale. The pattern of the graphite showed that it outlined the pre-existing eutectic cementite. In the vicinity of this graphite considerable lakes of ferrite occurred, and interlocked in circles of graphite were areas of cementite.

This will be apparent from a close examination of Figs. 15 and 16 in which the cementite areas are marked *C* and the ferrite areas are marked *F*. It is suggested that the graphite must have formed after the cementite areas, and may have resulted from the graphitization of this cementite together with the formation of hypereutectoid graphite. The ferrite areas must have formed during or after the eutectoid transformation as it would be difficult to envisage carbon-free austenite in contact with cementite or graphite under these conditions of cooling.

In all the experiments described so far in this series it was felt that manganese and the resulting manganese sulphide were complicating factors. Accordingly, a synthetic melt was arranged using a special sample of Swedish wrought iron which had a very low manganese content. Four ingots were cast from a high-frequency induction furnace. Details of the charge have been given in the section dealing with melting procedure. The results of the chemical analysis of these four samples are given in Table V.

TABLE V.—*Chemical Analyses of Ingots from Induction-Furnace Melt.*

Sample.	Mn, %.	S, %.	Cu, %.
1F3	Nil	0.222	0.74
1F4	Nil	0.249	1.49
1F5	Nil	0.229	2.90
1F6	Nil	0.242	5.93

Samples 1F3, 1F4, and 1F5 all contained ferrous sulphide associated with the deep brown phase previously noted. Fig. 18 shows a typical aggregate in sample 1F4. With increasing copper content the amount of ferrous sulphide decreases until in sample 1F6 with 5.93% of copper, only very small amounts are present. In samples 1F3, 1F4, and 1F5, there is some indication that the eutectic structure may exist in the deep brown phase and this was more apparent but still difficult to resolve in sample 1F6. Fig. 19 shows a typical deep brown phase (upper) in sample 1F6 with a hardly resolved eutectic structure. A ferrous sulphide aggregate (lower) is also shown. In the absence of manganese it is felt that this indicates (together with the previous evidence) the formation of a double sulphide or a solid solution of Cu_2S and FeS , and also the possible occurrence of a eutectic of this phase and the bluish Cu_2S . It would also appear that MnS and Cu_2S may form a continuous series of solid solutions, but unless the manganese is very low and the sulphur and copper contents are very high, no massive Cu_2S will be formed. Quite obviously, manganese has a much greater affinity for sulphur than has copper.

The Chromium Series.

An examination of the literature indicated some considerable knowledge of the effect of chromium on the sulphides in steels and pure iron. In the correspondence on a paper by Matuschka,¹³ Portevin pointed out that sulphur may form compounds with chromium, particularly in the presence of oxygen, giving probably a rose-coloured oxy-sulphide of iron and chromium. Urban and Chipman¹⁴ have prepared a synthetic iron-carbon alloy adding ferro-chromium and iron sulphide and they found inclusions consisting of alternate lamellae of parallel narrow bands. They say that this indicates the solubility of two sulphides at melting temperature—the one being precipitated in cooling. The tan-coloured phase they suggest is rich in FeS and the grey phase rich in Cr_2S_3 . Löfquist¹⁵ reported chromium sulphide in steel to be light grey and he identified a chromium-sulphide/oxide eutectic. Monypenny¹⁶ has referred to the difficulty of sulphur-printing chromium steels, and he says that unless the manganese content is well over 0.5%, the sulphur exists mainly as chromium sulphide. Schafmeister and Moll¹⁷ found that melts with high chromium and sulphur contents contained globular sulphides, the smaller particles being anisotropic and the larger particles isotropic under polarized light between crossed nicols. Both types were grey and these investigators suggested the isotropic phase to be chromium sulphide and the anisotropic phase to be iron sulphide containing chromium sulphide. Portevin and Castro¹⁸ have illustrated the occurrence of a special phase in the sulphides of 1% chromium steels. This phase is light grey and occurs in triangular crystals associated with manganese sulphide and also as a eutectic with this compound. These investigators found that the sulphides in low-chromium steels resembled in tint the manganese sulphide containing iron sulphide in solid solution, and the sulphides in high-chromium steels to resemble pure iron sulphide. The sulphides of chromium were found to be relatively inert to the usual etching reagents for sulphides. The iron/chromium/chromium-sulphide/iron-sulphide system has been studied by Vogel and Reinbach.¹⁹ Iron sulphide (FeS) and chromium sulphide (CrS) show complete miscibility in the liquid condition for the system FeS-CrS .

With chromium contents up to about 1% no abnormal sulphides have been observed by the author in iron with sufficient manganese to balance the sulphur content, but in chilled rolls of heavy section having manganese contents of the order of 0.3% and chromium contents of 1% and above, sulphide aggregates exactly resembling that illustrated by Portevin and Castro (*loc. cit.*) have been observed and one is shown in Fig. 20. The dark

phase is manganese sulphide in which a fine eutectic-like structure can be seen. The lighter phase has a light grey colouring.

For this series nine melts were carried out covering the range 0.74–28.53% of chromium. Low-carbon ferro-chromium was used. The chemical analyses are recorded in Table VI. As far as the general microstructures were concerned, all the bars were typical of white irons with the chromium contents indicated. Up to 8.54% of chromium the pearlite became progressively finer; at 11.84% the carbides became slightly angular; at 15.12 and 17.31% the carbides had the typical angular appearance of iron–chromium carbide in very fine pearlite; and at 28.53% of chromium, chromium–iron carbides were present in an *a* matrix with no pearlite.

TABLE VI.—*Chemical Analyses of Samples in the Chromium Series.*

(Pig iron *A* used in each case.)

Sample.	T.C, %.	Si, %.	Mn, %.	S, %.	Cr, %.
<i>MS/566</i>	2.98	0.70	0.36	0.624	0.74
<i>MS/568</i>	3.11	0.79	0.36	0.701	1.39
<i>MS/569</i>	3.04	0.62	0.19	0.347	1.94
<i>MS/570</i>	3.01	0.62	0.23	0.498	5.06
<i>MS/617</i>	3.14	0.88	0.20	0.447	8.54
<i>MS/618</i>	3.16	0.85	0.21	0.408	11.84
<i>MS/623</i>	3.47	1.30	0.20	0.484	15.12
<i>MS/625</i>	3.20	1.00	0.20	0.275	17.31
<i>MS/591</i>	2.83	0.98	0.19	0.386	28.53

Sample *MS/566* with 0.74% of chromium showed sulphide aggregates consisting of manganese sulphide and iron sulphide. Very fine greyish streaks were visible in some of the FeS areas and small, light grey spots were discerned in the manganese sulphide crystals. A typical aggregate is illustrated in Fig. 23. The dark phase is MnS and contains fine light spots. The light phase in which faint striations are visible is predominantly FeS.

Sample *MS/568* with 1.39% of chromium was essentially similar to sample *MS/566*, but the striations in the iron sulphide were more clearly developed and—confirming the observations of Urban and Chipman—appeared to be alternate lamellae of a light grey phase and a tan-coloured phase. The spots in the manganese sulphide were similarly light grey (Fig. 24).

Samples *MS/569* and *MS/570* with 1.94% and 5.06% of chromium, respectively, are again similar to the previous ones, but the striations in the iron sulphide are more pronounced still, and, in general, this phase appears grey-blue instead of the usual tan colour. A typical example of the striated structure in sample *MS/570* is illustrated in Fig. 25. The spotted structure is still present in the manganese sulphide (Fig. 26).

Samples *MS/617* and *MS/618*, with 8.54% and 11.84% of chromium, respectively, have relatively small amounts of manganese sulphide associated with a phase which appears light grey-blue to khaki. This phase is faintly doubly refracting under polarized light between crossed nicols and consists in each case of several differently oriented crystals, some of which are more khaki and others more grey. The shades of difference are very fine and it was found impossible to reproduce them photographically. Figs. 27 and 28 show typical sulphide aggregates in these two samples. In each case the dark phase is MnS.

Samples *MS/623* and *MS/625*, with 15.12% and 17.31% of chromium, respectively, were very similar and showed sulphide aggregates consisting of a small amount of manganese sulphide together with a grey phase and a khaki phase. A typical example from *MS/625* is illustrated in Fig. 29. The dark phase represents MnS, the khaki phase is shown medium-toned, and the grey phase is light.

Sample *MS/591*, with 28.53% of chromium, revealed sulphide aggregates consisting of a small amount of manganese sulphide and a phase which appeared to have various shades of khaki. This was found to be due to a faint reflex pleochroism—the crystals under plane polarized light absorbing more light for some orientations of the crystals with respect to the plane of polarization than for others. This is illustrated in Fig. 31. This khaki phase is undoubtedly the same as that found by Portevin and Castro in high-chromium steels. The reflex pleochroism clearly differentiates it from iron sulphide.

The Aluminium Series.

Little information was available in the literature upon the probable occurrence of aluminium sulphide or its complexes in steels or cast irons. Vogel and Hillen²⁰ have studied the iron/iron-sulphide/aluminium-sulphide/aluminium constitutional diagram. The existence of a FeS–Al₂S₃ solid solution was established and X-ray evidence confirmed the existence of the double-sulphide phase corresponding to FeS.Al₂S₃. Aluminium sulphide solidifies with a golden-yellow glassy appearance. Considerable liquid immiscibility of sulphides and metal was indicated.

In aluminium irons containing sufficient manganese to balance the sulphur, only manganese sulphide has been observed even for aluminium contents as high as 8%. When such irons also contained zirconium the orange-yellow to grey zirconium sulphide phase was present. This indicates that manganese and zirconium have a greater affinity for sulphur than has aluminium.

Seven melts were carried out in this series, four using pig iron *A* and three using pig iron *S*. The chemical analyses are given in Table VII. The

aluminium was added after the charge had melted in each case. As far as the general structure of these bars was concerned, they had normal microstructures typical of their alloy contents. A discussion of these complex structures would be irrelevant to the subject of this paper. Briefly, *MS/584*, *MS/311*, and *MS/312* were normal white irons; *MS/586* and *MS/313* were grey, and *MS/587* was white, with the carbon in the form of aluminium-iron carbide. Any graphite which occurred in this series was of the medium-sized flake type.

TABLE VII.—*Chemical Analyses of the Aluminium Series Samples.*

Sample.	Pig Iron.	T.C. %.	Si, %.	Mn, %.	S, %.	Al, %.
<i>MS/584</i>	<i>A</i>	2.98	0.71	0.21	0.399	0.78
<i>MS/585</i>	<i>A</i>	2.58	0.75	0.20	0.309	1.67
<i>MS/586</i>	<i>A</i>	2.98	0.69	0.27	0.331	3.46
<i>MS/587</i>	<i>A</i>	2.75	0.67	0.22	0.158	7.77
<i>MS/311</i>	<i>S</i>	0.10	0.341	0.55
<i>MS/312</i>	<i>S</i>	0.12	0.381	1.07
<i>MS/313</i>	<i>S</i>	0.06	0.340	2.19

Samples *MS/584*, *MS/585*, *MS/311*, and *MS/312*, with 0.78, 1.67, 0.55, and 1.07% of aluminium, respectively, all showed what appeared to be manganese sulphide with no iron sulphide present. Samples *MS/313*, *MS/586* and *MS/587*, with 2.19, 3.46, and 7.77% of aluminium, respectively, all had sulphide in the form of round, translucent, dark green particles (Fig. 21). The translucency was manifest under ordinary vertical illumination by a diffused golden or olive-green area of indeterminate focus at the centre of each particle. Under polarized light these particles lit up with a golden or olive-green coloration (Fig. 22) for all positions of the stage, indicating that they were glassy or isotropic, and translucent to golden-yellow/olive-green light. These particles are probably aluminium sulphide, perhaps containing some manganese sulphide (which would be responsible for the greenish appearance) in solution.

SUMMARY AND CONCLUSIONS.

(1) The influence of nickel in amounts up to 20%, of molybdenum up to 2%, of copper up to 5.9%, of chromium up to 28%, and of aluminium up to 7.7%, on the sulphide phases in low-manganese, high-sulphur irons, has been studied.

(2) With the exception of nickel, all these elements can combine with sulphur (in the absence of sufficient manganese to form manganese sulphide) to give characteristic sulphides.

(3) In the cases of copper, chromium, and aluminium, definite sulphides may be detected.

(4) Nickel and copper behave similarly in

neutralizing the carbide-stabilizing effect of iron sulphide, but nickel appears to exert a stronger influence.

(5) With high sulphur and low manganese contents, the addition of nickel or copper can give rise to abnormal graphite structures possessing features suggesting graphitization after solidification.

(6) As far as commercial irons of to-day are concerned, the sulphides described may occur in the case of copper, chromium, and aluminium irons.

(7) No definite sulphide was attributed to molybdenum, although that element definitely had an effect on the mode of occurrence of iron sulphide when 2% of molybdenum were present.

(8) Either a solid solution of Cu_2S in FeS or a double sulphide of these two can exist in cast iron.

(9) A eutectic of this solid solution (or double sulphide) and Cu_2S may occur in cast iron.

(10) Cuprous sulphide (Cu_2S) may exist in varying amounts in solution in manganese sulphide in cast iron.

(11) Chromium sulphide (CrS) may occur associated with iron sulphide in striations or with manganese sulphide in a eutectiform pattern of spots.

(12) The grey chromium sulphide phase may be chromium sulphide with iron sulphide and/or manganese sulphide in solid solution.

(13) With approximately 30% of chromium, the chromium sulphide had a khaki colour and showed a faint reflex pleochroism. With chromium contents of this order the pleochroic phase replaced the iron sulphide completely.

(14) With low manganese contents aluminium sulphide (Al_2S_3) containing manganese sulphide in solid solution may occur in cast iron.

(15) In no case did pouring temperature appear to have any influence on the form of the sulphides in any of the compositions investigated.

(16) It should be remembered that the above remarks all apply to irons of very high sulphur and low manganese contents.

ACKNOWLEDGMENTS.

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JOINT DISCUSSION.

The following two papers were discussed jointly: "The Origin and Constitution of Certain Non-Metallic Inclusions in Steel," by J. R. Rait and H. W. Pinder, and "The Neutralization of Sulphur in Cast Iron by Various Alloying Elements," by H. Morrogh.

(Figs. A and B = Plate LXIV.)

Dr. J. H. WHITELEY (Consett Iron Co., Ltd., Consett): I think Dr. Rait and Mr. Pinder have presented an excellent paper and one that will prove most useful in dealing with very heavy inclusions which sometimes occur in steel. Such inclusions are often very difficult to identify with certainty and there can be no doubt that X-ray analysis provides a valuable means of attacking the problem. In my judgement these authors have painted somewhat too dark a picture of the effect of inclusions on the physical properties of steel. It is remarkable how well a really dirty steel will sometimes stand up to severe service conditions. Much depends on the class of steel, however, and on its hardness, as well as on the sizes and distribution of the inclusions. It is my experience that inclusions can cause the steelmaker much more trouble and loss than the user in that they often give rise to troublesome surface defects. There are three questions I would like to ask the authors. Firstly, what was the strength of the hydrofluoric acid they used and the period of immersion, for I note in one instance (Fig. 62) that silica does not seem to have been attacked by that reagent, which is rather surprising. Then I would enquire why the authors used alkaline sodium picrate rather than sodium hydrate. Thirdly, can they say how it comes about that aluminous particles tend to occur so frequently in stringers.

From a metallographical standpoint I find the paper by Mr. Morrogh to be one of great interest. The account given of the work which has so far been done on the sulphides of the several alloying

elements is, of itself, very welcome, and I am sure the observations recorded in the paper will be most useful to future investigators. I would especially compliment Mr. Morrogh on the excellence of his illustrations. It is sometimes extremely difficult to obtain a clear delineation of sulphide inclusions but, in that respect, the examples given in the paper leave nothing to be desired. I have only one question to ask concerning them; in Figs. 11 and 12 the composite inclusion is surrounded by a white border. Is that substance copper or carbide? If the latter, then it looks very much as though the carbide was ejected from the sulphide during solidification so that, in the copper irons at any rate, carbide and sulphide may have been associated in the liquid state.

In dealing with the nickel irons Mr. Morrogh has advanced an explanation of a certain kind of graphite formation based on a possible change of the stabilizing FeS in the carbide to MnS as the iron cooled. Now, sample MS/520, which is the occasion of this suggestion, contained only 0.20% of manganese and I think it is a fair estimate that at least one half of that amount would at the outset exist as MnS, while a further quantity would be combined with the carbon, so that probably not more than 0.05% would be available for diffusion, on which any change from FeS to MnS must, of course, depend. From the work I have so far done on the subject I feel quite sure that if the FeS were contained in γ iron no perceptible increase of MnS would then occur during the relatively short time the casting took

to cool, for in steel manganese diffuses very slowly at high temperatures even when the gradient is steep. Whether diffusion is much more rapid in iron carbide I cannot say but, supposing that to be the case, there is still the question as to whether the carbide would part with its manganese, or, if that element diffused in from the outside, whether the iron of the carbide would not be displaced in preference to the iron of the sulphide. Nevertheless, the explanation Mr. Morrogh has put forward is a very interesting one and I hope he will endeavour to obtain evidence in support of it.

With regard to the effect of molybdenum on the sulphide inclusions Mr. Morrogh states that as much as 1.5% did not appear to influence their mode of occurrence. Yet it is well known that a low sulphur result is given by the evolution method even when only 0.3% of molybdenum is present in the sample. I would ask Mr. Morrogh whether he can account for that.

I noticed that Mr. Morrogh had no hesitation about FeS and MnS, but was very guarded in the way he described the new inclusions which appeared on adding the different alloying elements. Invariably he referred to them as phases, which seemed to me very advisable, but on coming to the summary and conclusions, I found that all such caution had been thrown to the winds, for there he says that the phases were, in fact, the sulphides, presumably unadulterated, of the added elements. That is very likely the case, but the reason for this change of attitude is by no means apparent. While Mr. Morrogh mentions the use of one or two chemical tests, none of which is precisely stated, he seems to have relied chiefly on colour and appearance for the identification of the phases that he finally asserts are sulphides. In so doing I cannot altogether blame him, for I have been in the habit of relying on the same features in dealing with FeS and MnS inclusions. Quite recently, however, I was very surprised to find that colour and appearance may not always be sufficient to distinguish with certainty between even those two sulphides and a short account of the observations which led me to that conclusion will not be out of place in discussing this paper.

I had occasion to examine a polished section of a bar which had been forged from a small block cut from the lower half of a free-cutting steel ingot containing 0.45% of sulphur, 1.0% of manganese, and about 0.10% of carbon. In forging the block a reduction of $\times 4$ was given and I expected to find some FeS in the bar but none was to be seen. All the numerous sulphide particles had the same dove-grey colour and under both ordinary and polarized light they seemed to be identical in composition. A typical area in the section is shown in Fig. A. Apparently the inclusions there illustrated were all MnS,

but I noticed they were more opaque than that substance usually is, and so I applied a reagent in which I had known for some time past that the solubilities of MnS and FeS were widely different; it consisted of a 10% solution of chromic acid in water. Immersion of the polished specimen in it for 10 min. at room temperature suffices to remove all MnS inclusions leaving dark cavities, while FeS remains unattacked even when immersed for 1 hr. or more. I had used this test on several samples containing FeS inclusions, including one sent to me by Dr. Desch of pure iron to which about 0.05% of sulphur had been added, and the result was always the same; no attack of the FeS particles was to be seen. On boiling the specimens in the solution for 10 min., however, the FeS was rapidly dissolved. Now, after the free-cutting steel specimen had been immersed for 10 min. in the reagent at room temperature I found that, while most of the inclusions had dissolved, a few, generally in clusters, were unaffected. Fig. B shows the area seen in Fig. A after that treatment. The result was exactly the same after immersion for 1 hr. and it was not until I had boiled the specimen in the solution for 10 min. that the resistant inclusions disappeared.

Thus I had encountered inclusions which looked like MnS and behaved like FeS. Subsequently I discovered, on examining a cupric etched section taken from the ingot itself, that such inclusions invariably occurred in or very near the local segregates, just where yellowish FeS is situated when it is present in that class of steel. Moreover, several tests, including sulphur printing, showed that these inclusions were genuine sulphide and not oxide of any kind. The fact that, without exception, all the inclusions in the segregated areas were insoluble in the cold reagent is of itself, I think, a sufficient guarantee that most if not all these resistant particles with the same colour as MnS were actually a sulphide. This observation seems to indicate that even in dealing with a common inclusion like MnS care may be needed at times in identification. I may add that I have found two or three reagents in which the rate of solution of the MnS particles in ordinary steels sometimes varies considerably, although not so widely as in the above instance.

Mr. D. A. OLIVER (Messrs. William Jessop & Sons, Ltd.): I should like to pay a tribute to the enormous amount of work which must have gone into both these papers. The art of preparing these sections is not an easy one, and it means repeated trials, and repeated polishings to expose fresh surfaces. I think that Mr. Morrogh's pictures are marvellous. Whether that is because I know less about cast iron than steel I do not know, but at any rate they are very fine pictures

indeed. Some of the photographs in the paper by Dr. Rait and Mr. Pinder are also, I think, fine examples of some very difficult inclusions.

I think I might disclose that Jessops could not produce all these inclusions themselves. A year ago I thought that Jessops were the only steel company that had admitted that it ever had experienced the incidence of non-metallic inclusions, but having reached that point we went further and hunted in other makers' steels for inclusions that we could not produce ourselves. That is one reason why the account given in the paper is as complete, I think, as any account given in a single paper before.

There is one aspect of this work which I should like to emphasize. I think that the study of inclusions over the next few years is going to become important from an entirely different angle, namely, that of machinability. With world competition in engineering, and with a growing knowledge of the materials which we are handling, there is going to be a greater emphasis on the economics of machining. We all know that with growing experience we can tolerate certain inclusions provided that they do not outcrop at critical positions or interfere with essential critically polished surfaces, so that after that our main concern is whether they affect the material at all. I leave aside the question of the effect on fatigue strength, because that is another story; but from a production point of view they very greatly affect production and engineering economics. Some types of inclusions are known to be capable of taking the edge off a high-speed-steel tool or of causing undue wear in carbide tools, and from that angle I am sure that these studies will have an important part to play in future work on tool performance.

Speaking more specifically, I think that aluminium stringers are probably the most devastating single cause of trouble in machining. After that there are certain glassy silicates which are harmless, but which if they have a single nucleus of alumina or silica appear to be very much more harmful. I throw out these suggestions as a side-issue to these very important and interesting detailed investigations on inclusions themselves.

The PRESIDENT (Dr. C. H. Desch, F.R.S.): When the first paper by Mr. Morrogh appeared some years ago, we were all greatly struck by the perfection of his specimens, and naturally wondered what kind of special technique he was using. The published paper did not seem to indicate anything very novel, and I remember going round to his laboratory to see what his methods were. I found that they did not differ very greatly from the methods which many of us had used for years, and that proved that the real difference was in the operator. I think that if

most of us—even those who have had, as I have, well over forty years of experience in polishing specimens—tried to prepare specimens to produce the photographs given in this paper we should not succeed. We all know how graphite particles tend to tear out in the course of polishing, but Mr. Morrogh is always able to preserve not only the shape of the graphite particle but even its internal structure. We have to congratulate him on his extraordinary skill.

With cast iron it is even more difficult than with steel to retain all the inclusions in the course of polishing. We can see now that the value of this kind of examination is very high, but its value depends entirely on the amount of skill shown in preparing the surfaces. When they are prepared as well as these, it is possible to get a good deal of information from their mere appearance, and without applying etching reagents. On the other hand, a badly polished specimen will not give all the information wanted even with the most elaborate arrangements of differential etching.

One method which I think might be used a little more than is the case is one which we used at the National Physical Laboratory in studying sulphide inclusions, and that is to take a polished specimen and apply to it a glossy gelatine-coated paper impregnated with some reagent which would react when an acid was applied. In that way, on pressing the impregnated paper on to the surface of the metal and allowing sufficient time for chemical action to take place and then peeling the paper off, we could examine the contact print under the microscope, thus getting a replica of the surface and obtaining a great deal of information. The specimens have to be very well prepared, but with the present micro-chemical technique there are a good many reagents which can be used for identifying inclusions in that way.

Dr. Whiteley does not want us to be too much afraid of inclusions, but every manufacturer would agree that if he could make a clean steel he would be very pleased to do so, and I am sure that many users would like to have their steels quite clean. It is perhaps within the recollection of some members here that when a good many years ago we had a discussion on the effect of inclusions, one of the big steelmakers received an order immediately afterwards for so many tons of special steel "free from inclusions."

Mr. R. WHITFIELD (Incandescent Heat Co., Ltd., Smethwick, Birmingham): I was particularly interested in the paper by Mr. Morrogh, but a little surprised and disappointed that the study was not pursued with regard to the physical characteristics of a sulphur-bearing cast iron, because I feel sure that if we can control the sulphur there is a possibility of making it beneficial. I should like

to see work on sulphur-bearing cast iron pursued, therefore, with a view to obtaining some of the important physical results that are so much needed.

I have tried to control the sulphur, particularly with malleable castings, but have found that the sulphur could not be depended upon to come out with any accuracy. An acid lining kept in the ladle, with sodium carbonate, showed an improvement, but more definite and controllable results were obtained when the ladle was basic-lined. Then I tried lining the whole cupola basically, with the result that there was a fair measure of success in controlling the sulphur *via* the slag if the source of the sulphur was known. Moreover, the acid-lined cupola had to be repaired after every heat, but 40 or 50 heats have been carried out in the basic cupola without touching the lining. That is one way of controlling the sulphur within the material.

I think that some means of dealing with the sulphur other than by causing turbulence, which gives a tremendous number of blow-holes, will have to be found.

Dr. J. H. CHESTERS (The United Steel Companies, Ltd.): We have tried to tell what proportion of the inclusions in steel actually come from the refractories. The preliminary results are hardly in a state to be published, and we want to do more check work, but they suggest that in the ordinary way the proportion of the dirt coming from the refractories is very small, in some casts probably only 1%. But there is always one ambiguity, and that is whether, when we find alumina, usually as corundum, it can have come from the refractories. I should like to ask Dr. Rait and Mr. Pinder whether they have any confidence when they say that such-and-such alumina came from aluminium. If one gets glassy inclusions high in alumina when no aluminium has been added the alumina must have come from the refractories, but when aluminium has been added are they sure that the alumina which they

find has come from aluminium and not from the dissociation of the mullite in the firebricks?

Mr. J. G. PEARCE (British Cast Iron Research Association, Birmingham): I have no special remarks to make on the papers, but the President's remarks on microscopic technique stimulate me to say that in the British Cast Iron Research Association we are absolutely convinced that the microscope as a metallurgical instrument has not yet been exploited to the full extent of its possibilities. If anybody is interested in the technique that we adopt we should be delighted to show it. We feel, however, that with further study and development many of the results for which metallurgists are now looking to X-ray diffraction methods or the electron microscope can be achieved with the visual microscope with properly worked-out methods.

That is one reason why some time ago we suggested that the Institute might care to foster some sort of metallographic or microscopic study group which would pursue the matter further. We were not particular as to the precise mechanism, as long as it fitted in with the Institute's organization, but both ferrous and non-ferrous metals are included. I should, however, like to underline our conviction that microscopic methods still fall far short of the ends to which they can be taken, and are capable of throwing a good deal more light on problems such as are raised in these two papers.

The PRESIDENT (Dr. C. H. Desch, F.R.S.): I entirely agree with Mr. Pearce. I do not think that the microscopical method has been used to its full extent as yet. There is a question which I should like to ask on this point. Mr. Morrogh speaks of using the polarized-light method, which is very valuable. It is not always easy to get nicol prism attachments for the microscope for this kind of work. Has he made any use of polaroid films, which are much simpler to attach, for getting these polarized-light effects?

JOINT CORRESPONDENCE.

Professor ADAM S. SKAPSKI (Institute for the Study of Metals, University of Chicago, U.S.A.) wrote: Mr. Morrogh should be congratulated upon his work which—among other items—produces microscopic evidence for the presence of copper sulphide in copper-bearing cast iron, and in this way calls to the metallurgist's attention the fact that copper may play a greater rôle in the equilibria in the steelmaking process, where the affinity relations are still more favourable for copper sulphide—a fact which had been hitherto overlooked.

As for Mr. Morrogh's statement that "no information was discovered in the literature which had any direct bearing on this investigation upon the mode of occurrence of sulphur in cast iron and steel," I would like to call his attention to the paper "Copper Sulphide in Steel" by A. Skapski, A. Kotlinski, and W. Goslawski*.

In the quoted paper a method of electrolytic extraction of non-metallic inclusions was described, allowing of the quantitative determination of iron, manganese, and copper sulphides separately. The analytical results were adduced

* *Extraits des Annales de l'Academie des Sciences Techniques a Varsovie*, 1939, vol. 6, p. 23.

which showed that in the steels investigated (containing usual amounts of copper) the sulphidic inclusions consisted mainly of manganese and copper sulphides; and, finally, thermodynamical considerations were presented to the effect that—at the temperature of the steelmaking process—the affinity of copper for sulphur is much greater than that of iron and possibly even of manganese.

The analytical method of separating individual sulphides from steel is now being further developed and new measurements of the affinity of sulphur for iron and the iron alloying elements are being made by N. H. Nachtrieb, E. M. Cox, and the writer at the Institute for the Study of Metals, University of Chicago. The results will be published shortly.

Mr. A. ALLISON (Sheffield) wrote: I am interested in Mr. Morrogh's study of sulphides in alloy cast irons, because I have photographed many specimens of nickel-chromium irons with attention to the sulphides present.

Is Mr. Morrogh correct in claiming that the structures found are typical, because I have observed that in the same specimen some sulphides may exhibit complexity and others an apparently simple compound?

Moreover, I have found that some crystals of MnS occur in the carbide areas and others in the martensitic areas. The latter are often in a white matrix, similar to Mr. Morrogh's Figs. 6 and 9.

Mr. Morrogh does not refer to the regular rhomboidal shapes of the sulphides, nor to the skeleton or anchor-like shapes frequently found, although the specimens under my observation have mostly been taken from much larger pieces, namely, chilled iron rolls.

Would Mr. Morrogh agree that these characteristic shapes occur only with higher Mn/S ratios?

The statement that Ni_3S_2 has a freezing point of 790°C . is surprising, in view of the well-known evidence that MnS crystals are solid in molten iron, unless the nickel sulphide remains in solution and falls out after primary solidification.

Although it is claimed in the conclusions that the pouring temperature appears to have little effect on the form of the sulphides, have the much higher temperatures of the rich alloy irons been taken into consideration?

The paper shows clearly that manganese has the strongest affinity for sulphur of the alloys examined, and since manganese is usually present in cast iron in amounts adequate to deal with the sulphur contents, the statement that sulphur must be regarded as a useful alloying element can hardly be considered as proved.

It would have been useful if some method of overcoming the unsoundness of the test-bars had enabled good mechanical tests to be obtained on such a wide range of different alloys.

The paper shows considerable advances in microscopic technique.

AUTHORS' REPLIES.

Mr. H. W. PINDER wrote in reply: In answer to Dr. Whiteley's first point, we used a 10% solution of hydrofluoric acid, and the etching periods varied considerably, because obviously we did not want to cause too much initial destruction of the inclusions. The usual preliminary period was of the order of 30 sec., and often the specimen was replaced for further etching. With regard to the second reagent, alkaline sodium picrate was used in our case; there was no specific reason for using this, it just happened to be found that it was a very convenient reagent. We understand, however, that sodium hydrate is likely to be a little more violent in its reaction.

We have met a number of examples of surface inclusions which are commonly described in the literature as sand spots, and there again we have been able to trace and link them with refractory materials.

Dr. Whiteley thought that we had painted a dark picture. All we can say is that we have shown not only what can happen, but also what actually does happen by way of extraneous contamination. The great comfort for the steel-makers is that it is not always their fault when dirty steel is produced.

Mr. MORROGH wrote in reply: Before replying to the detailed points raised in the discussion I would like to thank Dr. Desch, Mr. Oliver, and Dr. Whiteley for their kind appreciation of this work.

Dealing with the questions raised by Dr. Whiteley, I can confirm that the apparently white phase surrounding the sulphide complexes in Figs. 11 and 12 of the paper is carbide (cementite). This carbide phase appears very much brighter than the ferritic matrix because the matrix contains an appreciable amount of unresolved secondary copper which gives it a dark appearance. From the close association of carbide and sulphide in these irons it would seem unwise to go beyond the inference that during solidification they segregate together from the liquid, and so occur in juxtaposition. I agree with Dr. Whiteley that the validity of the explanations suggested for the unusual graphite formations illustrated in Figs. 1 and 2 and 13 to 17 must depend upon the speed at which the reaction $\text{FeS} + \text{Mn} \rightleftharpoons \text{MnS} + \text{Fe}$ can proceed. As Dr. Whiteley points out, this may be determined by the ability of manganese to reach the iron sulphide by diffusion. It is felt, however, that

the occurrence of graphite so obviously taking its shape from eutectic cementite, together with the existence of associated graphite spherulites, can be taken as an indication that the graphite has formed by carbide decomposition after solidification. This implies that the carbide becomes less stable with decreasing temperature, whereas carbide usually is more stable at lower temperatures. A detailed discussion of this point is not relevant to the main topic of this paper, but the matter will be dealt with more fully in another paper to be published shortly.

The methods used for the investigation described in this paper do not lend themselves to the definition of the purity of the sulphides observed, but only to the identification of the main types of sulphides present. It is most probable that in nearly all cases we are not dealing with pure manganese sulphide or pure iron sulphide, but rather with manganese sulphide containing iron in solution and iron sulphide containing manganese. Even when no definite new sulphides were observed, as in the cases of nickel and molybdenum, it is conceivable that these alloying elements were to some extent dissolved in the manganese-sulphide-rich and the iron-sulphide-rich phases. The influence of molybdenum upon the estimation of sulphur by the evolution method may be explained on these grounds. It can, however, be stated that no special sulphides of molybdenum were observed and that all the sulphide phases occurring in the molybdenum-containing irons were either essentially iron or manganese sulphides.

For the study of sulphide particles in cast iron the author prefers to avoid the use of etching reagents for their identification, since misleading results may frequently be obtained, particularly when the metallic matrix is highly alloyed. No difficulty has yet been experienced in differentiating manganese-sulphide-rich particles from iron-sulphide-rich particles in unalloyed cast irons; there is usually a marked colour difference, careful observation under polarized light usually indicates the anisotropy of the iron sulphide phase, and final confirmation can be obtained, if necessary, by heat-tinting, when the manganese sulphide can be made to take on a white coloration and iron sulphide a purple coloration. These remarks are based on observations upon cast irons and not upon steels, of which the author's experience is limited. It should be observed that the manganese and sulphur contents (1.0% and 0.45% respectively) in the steel referred to by Dr. Whiteley represent a combination rarely, if ever, obtained in cast irons or pig irons. In these high-carbon alloys, at normal melting and pouring temperatures, 0.45% of sulphur could be obtained only with very low manganese contents.

Dr. Desch refers to a modification of the

sulphur-printing technique. This is useful for the study of the distribution of sulphur, particularly in steels, but the author finds this method of limited use for cast-iron sections, particularly when the irons are graphitic. In the work described in this paper the author was concerned with the type of sulphides, rather than with the distribution of the sulphides. Dealing with the question of the metallurgical polarizing microscope, the author has used both nicol prisms alone and polaroid discs alone and also combinations of nicol prism and polaroid. With the old type of polaroid, using a disc placed in the illuminating train as polarizer and a disc as analyser placed either behind the vertical illuminator or in the eye-piece, a marked red coloration was obtained when the two discs were crossed. A suitable compromise, however, was achieved by the use of a nicol prism in the illuminating train and a polaroid disc as analyser. With the latest form of polaroid, the red coloration is not present and two polaroid discs can be satisfactorily employed. If nicol prisms are obtainable, however, the author still prefers to use one as a polarizer in the illuminating train and to have a polaroid disc behind the vertical illuminator as the analyser. Unless infinity-corrected objectives are available, it is not satisfactory to use a nicol prism as the analyser behind the vertical illuminator.

Mr. Whitfield's comments are timely in pointing out that much further work is required upon the influence of sulphur in cast iron and he has referred to the problems relating to desulphurization. It is the opinion of the author that the full metallurgical possibilities of cast iron will only be realized when advantage is taken of the fact that sulphur can be present in cast irons in several different forms, for instance, as titanium sulphide, as zirconium sulphide, as a copper sulphide, as an aluminium sulphide and as chromium sulphide, in addition to the well-known manganese and iron sulphides. It is possible that the element can exist in still further combinations when other suitable alloying elements are present. The effect of sulphur is frequently indirect and is manifest by its influence on the course of the major phase changes, such as the formation of graphite. By changing the mode of occurrence of the sulphur, that is, by arranging its combination with other elements, new types of structure may be achieved for cast iron. This paper was intended to record the results of a preliminary exploration of this field.

The author is indebted to Professor Skapski for pointing out that the valuable work carried out in Poland upon the electrolytic separation of sulphides from steels had been overlooked. Professor Skapski and his colleagues have demonstrated the presence of copper sulphide in steels,

with adequate manganese normally to fix all the sulphur as manganese sulphide, and which contain as little as 0.2% of copper. Furthermore, evidence is produced indicating the affinity of copper for sulphur to be greater than that of iron at steelmelting temperatures. It can be inferred from these results that the manganese sulphide in copper-containing cast irons will contain appreciable amounts of copper, even when sufficient manganese is present to balance the sulphur. This point is confirmed by the observation made in the paper that under certain conditions in the presence of copper, manganese sulphide takes on a blue coloration.

Replying to the contribution made by Mr. Allison, the author is satisfied that the photomicrographs and descriptions given illustrate the typical features of the samples investigated. It is possible that the sulphide phases described differ considerably from those observed by Mr. Allison, since the compositions studied are not typical of commercial irons. It is true that the sulphides do not always occur associated with the

eutectic carbide phase and a few particles in most samples are associated with the primary austenite dendrites. However, the generalization that the sulphides tend to segregate with the eutectic carbide is valid. No reference was made to the "rhomboidal" or "anchor-like" shapes because these did not occur in the samples examined. A full description* has previously been given of these structures and the author would confirm that they tend to occur in irons with higher manganese contents than those used in this investigation. With regard to nickel sulphide, it should be noted that no evidence of its occurrence was obtained. The highest pouring temperature used in this investigation was 1480° C. and few if any alloyed cast irons are poured at temperatures much in excess of this figure. Mr. Allison suggests, because of the predominating affinity of manganese for sulphur, that the usefulness of sulphur as an alloying element is limited. In order to utilize sulphur in the alternative combinations it would be necessary to use lower manganese contents than normal.

* H. Morrogh, *Journal of The Iron and Steel Institute*, 1941, No. I., pp. 207 P-252 P.

Discussion on THE REMOVAL OF HYDROGEN FROM STEEL.

BY PROFESSOR J. H. ANDREW, D.Sc., H. LEE, B.Eng., Ph.D., A. K. MALLIK, B.Met., B.Sc.,
Ph.D., AND A. G. QUARRELL, D.Sc., F.Inst.P., F.I.M. (THE UNIVERSITY, SHEFFIELD).

Paper No. 22/1946 of the Alloy Steels Research Committee (submitted by the Hair-Line Crack Sub-Committee).

This paper was included in the programme for the Autumn Meeting of the Institute held on 13th and 14th November, 1946, and will be found in the Journal of The Iron and Steel Institute, 1946, No. 1., pp. 67 P-113 P. A synopsis of the paper is given below :

SYNOPSIS.

A systematic investigation of the removal of hydrogen from a number of steels under isothermal conditions has been carried out, and it is shown that for all steels the rate of removal in the intermediate range is high, and that for certain steels there is also a peak on the removal curve corresponding to transformation in the pearlitic region. The law governing hydrogen removal in the austenitic range has been determined experimentally, and the empirical relationship supported by theoretical treatment. The effect of transformation upon the removal of hydrogen is illustrated, and the effect of specimen size is also dealt with. It is shown that small partial pressures of hydrogen surrounding the steel at 1100° C. exert a considerable retarding effect upon the removal of hydrogen, although, as might be expected, this effect becomes quite small at 650° C.

In the presence of hydrogen, the transformation of a nickel-chromium-molybdenum steel was retarded in the range 600-450° C., but little effect was observed at lower temperatures. Comparison of the rate of diffusion of hydrogen through similar specimens of different steels showed that alloying elements have little, if any, effect upon the diffusion constant. This was confirmed in the austenitic range by the results obtained for the law of hydrogen removal. The evolution of hydrogen on cooling was followed, and it was found that the maximum rate of evolution corresponded to the end of the thermal transformation.

The mechanical properties of a large number of steels have been determined after treatment in hydrogen and nitrogen, and it is shown that the embrittling effect of hydrogen is apparent in all cases where the hydrogen content is 1.0-3.0 c.c./100 g.

In connection with the work on the removal of hydrogen, much evidence has been obtained upon the formation of hair-line cracks under various conditions. It was found that such cracks could appear in the absence of transformation stresses, and that these stresses are important mainly in that they determine the particular crack distribution which results. Although no cases were observed of internal crack formation in the absence of hydrogen, certain specimens showed no cracks in spite of a high hydrogen content. The view of the hydrogen-rich constituent put forward in a previous paper has been modified, in that it is not now considered to be necessarily austenitic; it is realized that at the moment of crack formation the steel will be in an extremely brittle condition, owing to its hydrogen content. The exact nature of the hydrogen-rich constitution cannot be given, nor can a detailed explanation of hair-line crack formation be expected, until the much wider problem of low-alloy steels in general is more thoroughly understood.

DISCUSSION.

Mr. H. H. BURTON (English Steel Corporation, Ltd.): It gives me very special pleasure to be asked to open this discussion. The subject of hair-line cracks and their prevention has been very near to my heart for a number of years, and I have been in touch with the investigation of Professor Andrew and his colleagues from the very outset.

I should like also to congratulate the authors on what I think is a very fine piece of work, covering a very wide range, and to say how much those of us who have been associated with this work have enjoyed the collaboration with Professor Andrew, Dr. Quarrell, Dr. Lee, and Dr. Mallik.

One of the outstanding features of this paper,

and indeed of its predecessor, is the very clear demonstration of the relationship between transformations and the rate of hydrogen removal, and transformations which result in stresses and the occurrence of hair-line cracks. Before this work was started there were various allusions in written work, mostly coming from abroad, to such a possibility, and I think that many of us who had been engaged in alloy-steel manufacture had assumed that such a relationship between transformation stresses and hair-line cracks might be present, but some of us were very doubtful about the effect of hydrogen, which had been largely demonstrated by what were regarded by quite a number of people as artificial methods.

I should like to deal briefly, in connection with this, with a statement which occurs early in this paper where, while I understand perfectly well what they intend to convey, I feel that what is said may be misread and misconstrued by some readers. It occurs at the bottom of the first page of the paper, where the authors say :

"Although many workers have suggested involved heat-treatments for the prevention of hair-line cracks, little work appears to have been reported in which the effect of heat-treatment has been systematically explored from the point of view of hydrogen removal. The simplest methods suggested for the prevention of hair-line cracks have involved slow cooling of the billet or forging after hot-work, but the rate of cooling necessary for a given steel of a definite cross-section has been determined only as a result of experience. When a new steel has been introduced, much work has been necessary before the minimum heat-treatment for the prevention of cracks could be specified. Owing to the uncertainty of the hydrogen content of steel ingots and the complex nature of steelworks practice, it is extremely difficult to make a direct comparison between steels of different compositions and their susceptibility to hair-line crack formation. This may account for the divergent opinions expressed by prominent steel-makers as to the best treatment for the prevention of hair-line cracks in specific cases."

As all those present are not familiar with the history of the Hair-Line Crack Sub-Committee, it seems desirable that some explanation should be given of the circumstances which led to the commencement of Professor Andrew's researches.

Before these researches began, there were in Great Britain two views, radically different, concerning the cause of hair-line crack formation. According to one of these views, the cracks could be explained by thermal transformation stresses alone. The other view, on the other hand, was that hydrogen alone was responsible. There was also a third view, held rather tentatively by a

numerically smaller group, that both transformation stresses and hydrogen might play an important part.

At that time there was no reliable information, at any rate in Great Britain, dealing with the hydrogen content of normal steels, and especially alloy steels, and the effect of various heating and cooling cycles on the hydrogen content; and a small informal group of alloy-steel makers, which had been formed some time previously to discuss this problem and exchange notes, decided to invite Professor Andrew to undertake an investigation of the hydrogen problem, and especially in the first place to confirm the work of the Italians, Musatti and Reggiori. He undertook this work with enthusiasm, and in a comparatively short time the work of the Italians had been both confirmed and extended. To-day I believe that our knowledge on this subject is greater than that of any other country, and I say that quite seriously, though much still remains to be investigated.

In this brief historical review of our work I would add, commenting on the last sentence which I quoted, with reference to the divergent opinions as to the best heat-treatment for the prevention of hair-line cracks, my own views concerning these divergent opinions. I believe that 90% of this divergence in opinion is due to the difference in the size of the alloy-steel articles with which the different firms have to deal, plus the fact that all the comparisons have not been made (this is in the past) on steels at the same stage in manufacture. I should like to emphasize this, because it is most important.

It is quite useless, as can be seen from the work published here on the removal of hydrogen by different heat-treatments, to compare the hair-line crack susceptibility of a steel billet which has been cooled for the first time through the transformation range after the ingot has been cast—that is to say, taken hot to the forge or rolling mill—with another in which the ingots have been allowed to cool down slowly and remain on the floor for a few weeks and then taken up and rolled. The susceptibility is not comparable in any way. That has often misled people into thinking that steel X was less susceptible than steel Y, whereas another manufacturer who studied the susceptibility in steels in exactly similar conditions has formed other conclusions.

Furthermore, I should like to point out that although we had no precise knowledge of the effect of different heat-treatments upon the removal of hydrogen, some of us—and especially those engaged in the manufacture of large masses of alloy steel, where the problem of hair-line cracks is much more acute—had been basing our precautionary treatments on a consideration of the transformations of the steel in question; and I suggest that the fact that this is a sound method of basing the

precautionary treatments is fully borne out by the results given in this paper. The authors themselves refer to the fact that the practice of cooling the specimens to 300° C. and subsequently reheating to 650° C. is soundly based.

There are several individual items on which I should like to comment. The first of these is the section dealing with the effects of specimen size, pp. 86 P and 87 P. The times there given would be quite impracticably prolonged, and I think that there must be something more in the removal of hydrogen in works practice than has yet appeared as a result of these investigations. It is too much to expect that it should have appeared so far. I say that because we do find that, in practice, in parts of large size, such as the 25-in. dia. billet referred to on p. 86 P, hydrogen can be removed or reduced to a safe level by cyclic heat-treatment, which sometimes involves reheating for forging plus various other cycles, such as refining, in less time than would be assumed to be possible from a consideration of the authors' curves, though it must be admitted in all fairness that they deal with hydrogen removal under isothermal conditions at temperatures such as 1100° C. in one case and 700° C. in another.

Personally, I am inclined to think—and this is a subject on which I am working at the moment, but unfortunately the work is not sufficiently completed to introduce it now—that the effect of cooling down to 300° C. and then reheating to some temperature above the heating transformation has a very profound effect, and it may be that a repetition of that transformation, both on heating and cooling, has effects which have not so far appeared.

The second point to which I should like to refer briefly is that of the embrittlement due to hydrogen, which is dealt with on pp. 103 P and 104 P. The suggestion here conveyed is that steels containing quite small amounts of hydrogen become very seriously embrittled; but those of us who have studied the properties of cores trepanned from masses of steel containing hydrogen as high as 6 c.c./100 g. at the time of testing have not found embrittlement of the same order, or at least I have not done so. There it is necessary to take into consideration the possibility that the specimen reheated in hydrogen may have been to some extent damaged on the exterior. I am not sure whether the authors reheated their tensile test-pieces in hydrogen after machining to test-piece size. If so, I should very much like to know whether they found any evidence of crazy cracking or other form of cracking of those specimens, apart from the cracks associated with the actual plane of fracture.

To give an illustration of what I am referring to, I have several records now of tests from forgings of 25 in. in dia., and over, in which the known hydro-

gen content at the time of testing was certainly more than 5 c.c./100 g., which have given elongations as high as 29% and reductions of area of 65%. I mention that because I think that there is something more in the problem of hydrogen embrittlement than can be derived from a consideration of specimens reheated in hydrogen, and it would be rather dangerous if it were to be thought that alloy steel containing hydrogen of the order of 1 c.c./100 g. was in a brittle and dangerous condition.

The third point is the statement by the authors that they have found hair-line cracks which are not accompanied by or due to transformation stresses. There is a reference to this on pp. 111 P and 112 P and in the Synopsis. The statement is largely based on certain apparently anomalous results obtained from specimens heat-treated isothermally, generally in what might be called the intermediate transformation range. I confess that I am very sceptical (a) whether some of these cracks are in fact hair-line cracks at all, and (b) whether the transformation which is stated by the authors to have been complete was in fact complete.

A particular case is that of the steel where reference is made to cracks forming after a certain time of isothermal treatment at 450° C., whereas no cracks occurred after a similar time of isothermal treatment at 400° C. To me, that seems to suggest very much that whatever the dilatometer showed, the transformation was not complete at 450° C. at that time.

I should like to suggest to the authors for the future, though I realize that to comply with my suggestion means the introduction of considerable difficulties in their work, that they should once again, as they have done in the past, consider whether the specimens they use, at least for the hair-line crack experiments, as distinct from the hydrogen-removal experiments, should not be sufficiently large to enable hair-line cracks to form by an air-cooling treatment instead of a water-quenching treatment. Looking at the illustrations on Plate II., for example, it is perfectly obvious that a great many of the cracks shown there are not hair-line cracks at all, and when you get those complications it is difficult to say whether you have hair-line cracks or not.

Take, for example, specimen (d) in the case of the specimens treated for 5 hr. (Fig. 12). Those look more or less like normal hair-line cracks, although in the ordinary way one would never get hair-line cracks in a specimen of that kind, even if the hydrogen content were very high; but in specimen (c) in the same series, thermally treated at 550° C., it is extremely difficult to say which of those cracks are quenching cracks, or perhaps quenching-cum-hydrogen-embrittlement cracks, and which are something more analogous to hair-line cracks.

I admire this work so much, and I feel so hopeful of the results that will come from it in due course, that I would appeal to the authors once again to consider whether a number of the experiments described in this paper might not be repeated on larger specimens, such as they have used in one previous research, cooled in air instead of quenched in water.

Dr. C. SYKES, F.R.S. (The Brown-Firth Research Laboratories): I should like to express my admiration for this work. The subject is a

from the cores of large alloy-steel forgings. The particular forgings were trepanned and one test was made on the core as quickly as possible after removal from the forging. An adjacent test-piece was tested after a treatment of 1 hr. at 750° F.

In Table A the diameter of the forgings is given in column (2) and is of the order of 20–30 in. in the body. In column (10) are the hydrogen contents corresponding to the various testing conditions. It will be seen that the stress-relieving treatment produces a substantial difference both in the hydrogen content and in mechanical

TABLE A.—Core Tests on 3% Chromium–Molybdenum Rotor Shafts.

H. and T. = Hardened and tempered. S.A. = Stress-annealed.

Cast No.	Body Dia., in.	Heat-Treatment.	Limit of Proportionality, tons/sq. in.	0.2% Proof Stress, tons/sq. in.	0.5% Proof Stress, tons/sq. in.	Maximum Stress, tons/sq. in.	Elongation, %.	Reduction of Area, %.	Hydrogen Content, c.c./100 g.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
25338A1	28½	H. and T. 670–680° C.	32	45	7	15	4.4
		+ S.A. 630–640° C.	37	45.2	9	15	5.7
25450A	31	H. and T. 675–680° C.	36	45.2	20.5	56	0.3
		+ S.A. 690–700° C.	31.8	35	38	46.8	19	42	2.8
25765A1	20½	H. and T. 670–680° C.	18.8	28.2	29.9	41.0	27.5	67	0.4
		+ S.A. 650–660° C.	27.8	36.2	37.0	46.2	22	56	1.2
25765A	23½	H. and T. 670–680° C.	25.8	32.9	33.9	43.8	28	68	...
		+ S.A. 650–660° C.	29.4	35.7	36.8	45.6	21	53	2.5
			25.4	33.1	35.0	43.8	26	67	...
96994A	28	H. and T. 670–680° C.	34.5	42.2	43.1	52.6	22	58	1.7
(6.6 c.c./100 g.)		Re-H. and T. 610–620° C.							
96994A1	31	H. and T. 670–680° C.	32.3	39.6	40.4	50.4	12	30	4.5
(6.6 c.c./100 g.)		+ S.A. 630–640° C.							
		+ 610–620° C. on test-piece	31.3	38.9	40.1	50.8	22	55	0.1
97491A1	31	H. and T. 650–660° C.	30.2	37.7	38.4	47.2	6	...	4.5
		+ 610–620° C. on test-piece	32.6	38	38.8	49.4	21	61	0.2
97504A	28	H. and T. 640–650° C.	31.8	37.6	38	47.6	19.5	42	3.5
97529A	28	H. and T. 630–640° C.	23.1	34.0	35.6	45.8	13	21	3.4
(7.5 c.c./100 g.)		+ 610–620° C. on test-piece	26.0	34.7	36.0	46.4	26.5	approx. 71	0.2
97529A1	31	H. and T. 650–660° C.	28.0	33.2	34.2	45.2	13	21	...
(7.5 c.c./100 g.)									

fascinating one, about which people have been arguing for many years, and about which they will probably continue to argue for a great many more. From the experimental point of view a number of special problems are involved. The investigator is dealing with a substance—hydrogen—which is disappearing from his test-pieces continuously and this introduces a number of difficulties. The authors have designed a number of most ingenious experiments in an endeavour to get over this type of difficulty and to a very large extent they have succeeded.

I have some results of the change in mechanical properties with hydrogen content which may be of interest. In these experiments the hydrogen was in the steel originally from melting, *i.e.*, it was not put in artificially. The test-pieces are taken

properties. In column (1) there are one or two figures for hydrogen in the liquid steel, immediately prior to casting. The particular heat-treatments that were given to the forging have reduced the hydrogen in the core to roughly half its original value.

It will be found that the elongations, except where the hydrogen is very high, *i.e.*, greater than 2 c.c., are good, but they are affected by the hydrogen content and once the hydrogen is removed still better results are obtained.

Similar effects are observed in carbon steels, but are of a smaller magnitude.

Fig. A is a curve which illustrates one of the problems in making large forgings and refers to an aspect which I think has tended to be overlooked by the authors. This figure is purely a mathe-

matical picture of what happens during heat-treatment to the hydrogen distribution of a cylinder having a uniform hydrogen content initially, the time-scale being a function of the diffusivity of the hydrogen and the diameter squared. In a large forging one would expect a definite hydrogen gradient from the outside to the inside; it is the inside which usually gives the trouble, and it is the inside which unfortunately has the most hydrogen. Hydrogen tests on samples cut at different distances from the centre of a forging substantiate the theoretical analyses.

that there is a strong indication that its effect becomes more marked as the tensile strength becomes higher, and I think that it would be useful if specific tests were carried out to elaborate this point in a quantitative manner.

With regard to the main body of the paper, the authors have made two important statements. First of all, they state that the diffusion of hydrogen in α iron is substantially independent of the alloy content. There is not a great deal of information in the paper supporting this statement, but it does agree with the work carried out by the Germans, and if we take it as being true it simplifies considerations relating to elimination of hydrogen. Personally, I am of the opinion that in carbon steels the rate of diffusion is somewhat higher than it is in alloy steels, but I cannot produce any precise figures to substantiate this.

The second point that the authors make is that hydrogen is removed very rapidly when the steel is transformed, *i.e.*, the diffusivity in α iron is much greater than in γ iron. If these two factors are taken together, I think we must agree that the rather peculiarly shaped curves given in the paper dealing with hydrogen evolution during the isothermal treatments which the authors have used, are really a very complex reflection of the transformation characteristics of the material somewhat distorted by the variation in diffusivity of hydrogen with temperature. They are difficult to interpret, therefore, in terms of possible works application. On the other hand, starting with the same two assumptions: (i) That the diffusivity of hydrogen is independent of the alloy content, but increases with temperature, in the α state, and (ii) that in order to get rid of hydrogen the material must be put into the α condition, then consideration shows that our various works heat-treatments are reasonably sound. For instance, the heat-treatments which we ourselves use are devised as follows. The material is cooled to ensure that it is transformed, the appropriate temperature being chosen, and then it is reheated to a temperature of 650° C., soaked to give rapid softening, and then cooled at a rate slow enough to prevent generation of substantial cooling stress. I think that this combination should get rid of hydrogen as quickly as possible, since at 650° C. one obtains very high diffusivity. There is in addition the point which Mr. Burton has raised, *viz.*, that of going above the change point, where, owing to the shape of the hydrogen distribution curve produced by the previous heat-treatments, reheating to austenite produces averaging between centre and outside, *see* Fig. A, and might be more effective regarding reduction of hydrogen at the centre. Although, therefore, the works treatments seem to be complicated, they are quite sound in the sense that cracks are prevented and they are

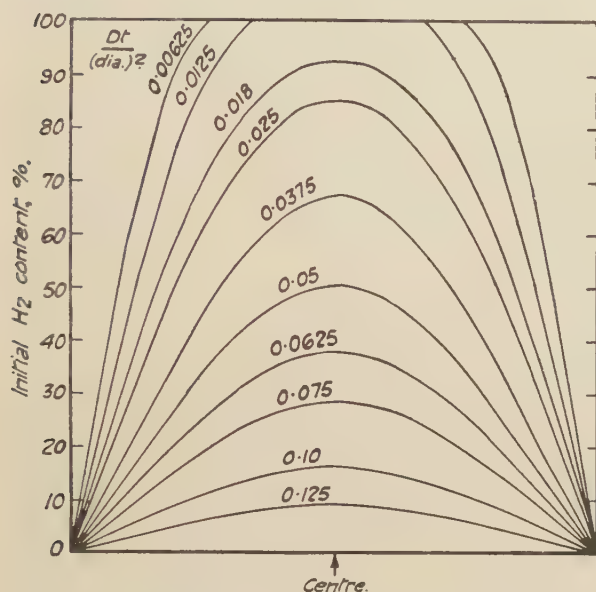


FIG. A.—Distribution of Hydrogen through Section of Solid Cylinder after Varying periods of Time.

I think that whilst the authors might be criticized (in my opinion unfairly) for introducing the hydrogen artificially, the results I have quoted show that even if it gets there by the usual method it has a similar effect on mechanical properties. On the other hand, I support Mr. Burton in suggesting that too much should not be made of this phenomenon. We all know quite well that in alloy-steel bar there is no difficulty in mechanical properties due to hydrogen because with sizes up to, say, 6 in., taking into account the normal period that it takes to manufacture such a bar, the hydrogen disappears and its residual effects are negligible. They are seldom noticed in ordinary routine testing. With large forgings the maximum stresses generally occur at a free surface, and, of course, as soon as a free surface appears one cannot retain the hydrogen, so that the normal ductility of a hydrogen-free material is obtained.

It is my opinion that if one examines the results which the authors have presented on the effect of hydrogen on mechanical properties, it will be seen

efficient in removing hydrogen. They have to do other things, of course, besides remove hydrogen, *e.g.*, to get the material soft in order to make it machinable and to minimize cooling stresses.

There is, however, one aspect which needs to be stated very clearly, and it is that, although these heat-treatments do prevent hair-line cracks, they do not eliminate hydrogen to values below those at which the authors claim to have produced hair-line cracks. I may refer to the figures which I have given in Table A, where hydrogen contents of up to 5 c.c./100 g. have actually been determined in finished forgings. An ingot of electric-furnace steel of, say, 1 ton in weight, will probably contain 6–7 c.c. of hydrogen per 100 g. when it is cast, and after a sound annealing treatment, it will be found that there still are 6 c.c. of hydrogen, or thereabouts, per 100 g. in the centre. This is in agreement, of course, with the authors' calculations. In other words the treatment has prevented the formation of hair-line cracks, but the hydrogen has not been eliminated; and that is something which we should keep firmly in our minds. The authors have indicated it implicitly; they have shown that to eliminate hydrogen from a 25-in. forging is more or less an impossibility from a practical aspect; but the fact of the matter is that such forgings are produced in very large quantities without hair-line cracks.

Thus, although hydrogen may be necessary for hair-line crack formation, large amounts of hydrogen can be tolerated without cracking if the treatments are appropriate, and it is just as important from the practical point of view to study methods of heat-treatment which permit large hydrogen contents with safety as to study methods of removing hydrogen.

The only practical way to ensure that the hydrogen content is low in the centre of large masses of steel, is to arrange that the steel is low in hydrogen when it is poured into the mould.

The authors say that the figures which they have given for the times required for the removal of hydrogen are probably conservative. I think that they may be optimistic, for the reason that in their experimental work the whole of the test-piece is used for the hydrogen determination; since there is a gradient in the test-piece, these hydrogen figures are average values. In practice, one is concerned with the hydrogen in the centre of the mass, so that it would appear necessary to multiply the figures which have been derived from average hydrogen contents by a factor of the order of 2. (See Fig. A.)

On the theoretical side, I still think that we are in the dark to a very great extent. I agree with the authors that high hydrogen concentrations are associated with hair-line cracks. I agree that the presence of hydrogen will tend to cause embrittlement and that it will cause pressure to be built up

within internal cavities. There is, however, the salient fact that an austenitic steel, which usually contains a good deal more hydrogen than a ferritic steel, never contains hair-line cracks. There is probably 50% more hydrogen there—it gets out much more slowly and yet it never produces hair-line cracks; on the pressure theory it should. It is true that owing to the higher solubility in γ per atmosphere pressure, the pressures will be lower in γ than α ; nevertheless they are still very high.

Again, hair-line cracks are often found only in the segregate zones and are then usually attributed to variation in transformation characteristics rather than to variations in ductility.

I definitely, therefore, do not subscribe to the statement made in the authors' conclusion (iii), that "hair-line cracks may occur in the absence of transformation stresses." I have read the paper carefully and I do not think that the authors have made out a really good case for that claim.

The authors' work has cleared up a number of outstanding points. My own view is that we now require some experiments which are specifically designed to find out whether ordinary cooling stresses in the presence of large amounts of hydrogen, as distinct from transformation stresses, can produce hair-line cracks, or whether the material merely becomes more susceptible to cracking in cooling. The authors' work, as Mr. Burton pointed out, is complicated by the fact that most of their test-pieces must contain substantial cooling stresses and many of the cracks illustrated are of the type one would associate with this type of stress rather than classify as hair-line cracks.

The separation of the effects of the two types of stress, together with a quantitative knowledge of the increase in the embrittling effect of hydrogen with increasing hardness should assist in further clarifying the hair-line crack problem.

Dr. N. P. ALLEN (National Physical Laboratory): Before the advent of the hydrogen theory of hair-line cracks, the transformation theory explained the fact that on the whole the steels which were most susceptible were those which had rather low transformation temperatures; but the transformation theory was not able to explain the heat-to-heat differences which were found between steels of nominally similar composition. The hydrogen theory was capable of explaining the heat-to-heat differences, but a difficulty at once arose in that the solubility of hydrogen and the rate of diffusion of hydrogen through alloy steels were found to be very much the same as in plain carbon steels, and consequently the hydrogen theory did not explain the greater susceptibility of the alloy steels.

This paper effects a reconciliation of the opposing views, because it becomes clear that the con-

dition for the easy removal of hydrogen is that the steel must first be transformed to α iron; so that the hydrogen theory is now capable of providing an explanation why certain types of steel are more susceptible than others.

Unfortunately, it turns out that the rate of escape is so low that it is almost impracticable to remove the hydrogen completely from very large forgings, from which two conclusions should be drawn. The first is that engineers should be brought to realize how enormously the use of a large section complicates the problems of the steelmaker, and be persuaded to exert their ingenuity to avoid the use of larger sections than are absolutely necessary in every case. Secondly, if you must have large sections it is highly desirable to see that the hydrogen does not get into the steel from the beginning, which means that attention has to be focused on the removal of hydrogen in the steelmaking process.

For that purpose there is need for a rapid means of determining the hydrogen content of the steel on the stage. If the results of hydrogen determinations are not available until long after the heat is complete, the improvement of technique will be slow. Therefore I feel that a good deal of effort ought to be given if possible to the problem of determining the hydrogen content of the steel while it is still molten and without allowing it to solidify, because the uncertainties of hydrogen determination are largely due to the fact that an uncertain proportion of the hydrogen escapes during solidification.

On the theoretical side, we seem to have a fairly good idea of how the hydrogen comes out of the material, but the connection between the hydrogen content of the metal and the appearance of the crack is little understood. We have in the paper examples of steels which are able to contain more hydrogen than others without showing cracks, and also a case where the same steel in two different conditions can bear two different quantities of hydrogen before the crack appears.

For a long time I tried to get these facts into order on the assumption that the hydrogen content and the hardness of the steel were the two factors concerned; but the data which we now have make it quite impossible to hold to that idea any longer. We have cases where the cracks are more abundant when the steel is martensitic, and other cases where they are more abundant when the steel is composed of intermediate transformation products. On the basis of the idea that the effect of hydrogen is due to the production of a high pressure in the steel, owing to the tendency of the hydrogen to escape from solution, importance might be attached to the limiting hydrogen content mentioned in the mathematical part of the paper. If we consider the limiting hydrogen content as hydrogen which is in some way more firmly bound to the steel than

the rest, then instead of putting for the mass of gas dissolved in the steel the ordinary equation:

$$m = S\sqrt{P},$$

we can substitute the equation:

$$m = S\sqrt{P} + a,$$

a being the limiting amount of hydrogen tightly bound to the steel. Then we find that the pressure which is developed when a certain quantity of hydrogen is in the steel is:

$$P = \left(\frac{m - a}{S}\right)^2.$$

This pressure will be extraordinarily sensitive to the value of a if a is at all near to m in its value.

Now, if we consider that we have two constituents in the steel which have respective solubilities of S_1 and S_2 , and volumes of V_1 and V_2 (the values of a for the two constituents being a_1 and a_2), the total amount of hydrogen in the steel is given by:

$$m = V_1(S_1\sqrt{P} + a_1) + V_2(S_2\sqrt{P} + a_2),$$

and in that case the pressure is given by:

$$P = \left(\frac{m - V_1a_1 - V_2a_2}{V_1S_1 + V_2S_2}\right)^2.$$

If the steel contains one constituent which has either a much higher value for the solubility constant than the average of the steel, or a much higher residual hydrogen content, its presence will have a very large effect on the maximum pressure that can be produced. Consequently it is very desirable to study the amount of hydrogen necessary to cause the cracks in relation to the constitution of the steel at the time when cracks are produced, and I therefore support Dr. Quarrell's suggestion that the transformation products and the nature of the transformation should be studied with some thoroughness.

Mr. A. J. K. HONEYMAN (Messrs. Colvilles, Ltd.): On p. 109 P the authors state that in the austenitic range in all cases the number of cracks is in accordance with the hydrogen content; the higher the hydrogen content the more numerous the cracks. They have also shown that the higher the temperature and the longer the time, the more hydrogen is removed. I should like to ask them how they can reconcile these statements with the slope of the boundary line in the austenitic range in their Fig. 44, for this shows that in the austenitic region the higher the temperature and the longer the time, the greater is the tendency to form hair-line cracks.

Moreover, the curve showing the beginning of transformation does not agree with the data in Table II. for the same steel. It is obvious, I think, from Table II. that some transformation

has begun at 550° C., since there the rate of hydrogen removal is much greater than it was at 600° C., but from the curve in Fig. 44 one would never suspect any transformation whatever at 550° C.

Still referring to Fig. 44, the authors state that transformation was complete in specimens quenched from 250–375° C., and that therefore transformation stresses could not have been the cause of the cracks observed. I would suggest that the authors' own work shows that it is quite probable that transformation is not complete. In Tables IX. and XI. there are two steels, K6 and N33, which after 5 hr. at 650° C. have respectively 0.22% and 0.44% of hydrogen. I do not suppose the authors would suggest that if the original isothermal treatment had been carried out for 7 hr., the hydrogen content would be nil, and we are thus forced to the conclusion that some change takes place during cooling to, or holding at, room temperature, as a result of which the remaining hydrogen is evolved on heating. I suggest that even in these steels, owing to the presence of hydrogen and possibly to segregation, traces of austenite are retained at 650° C. and transformed on further cooling. If this be so, then the 4S11 steel referred to on p. 98 P may not be completely transformed before quenching from 250–375° C.

I would submit therefore that the evidence contradicts the conclusion that hair-line cracks may occur in the absence of transformation stresses.

I was very much surprised to hear Dr. Quarrell's introduction to the paper, because it seemed to be an introduction to a different paper altogether. In his introduction, he laid great emphasis on the importance of isothermal transformation in the removal of hydrogen, but I do not think that anyone could say that that is emphasized in the paper; in fact, the authors seem almost grudging in their admission that transformation is accompanied by a rapid removal of hydrogen.

The rate of hydrogen removal under isothermal conditions and the removal of hydrogen in order to render the steel immune from hair-line crack formation are two quite different phenomena and the authors are in error in applying the results of the former as a guide to the latter. For example, Table IV. shows that isothermal removal of hydrogen is most effective between 450° and 250° C., and most ineffective at 550° C., the final hydrogen content after this treatment being 2.08 c.c./100 g., although cracks are absent. But all treatments finally end with the steel at room temperature and this figure of 2.08 c.c. includes the hydrogen evolved during cooling to, and in the course of one week at, room temperature. Thus, the final hydrogen content as reported in the various tables gives no indication of the final hydrogen content of the steel after cooling to room temperature. I venture to suggest that had another

column been added to the tables, giving only hydrogen content obtained after reheating, a somewhat different picture would have been obtained.

In the discussion of their results the authors state: "Although but little laboratory work has been carried out on the effect of cooling to 300° C., followed by reheating to 650° C., this method is based on sound theoretical principles." I suggest that these principles are, as has been pointed out by Dr. Sykes, first, that you must transform the austenite and, secondly, that you must heat that transformed austenite—that is, the ferrite—to as high a temperature as you can to get rid of the hydrogen. Indeed that is the principle of the method used to determine hydrogen. For practical purposes this is sufficiently achieved by transforming the austenite at the highest possible temperature, and retaining the steel at that temperature if it is above, say, 550° C. for as long as is necessary to remove the hydrogen or rather reduce it to less than 1 c.c./100 g. Only when the transformation is too slow in the pearlite range is further cooling and reheating necessary.

In the discussion of the previous paper referred to by the authors, I showed that isothermal transformation in the pearlitic range prevents the formation of hair-line cracks. Such treatment has the double advantage of putting the steel in the softest possible condition, thus facilitating machining and chisel-dressing and of being most economical in fuel.

The point that I want particularly to make is that in most of the low-alloy steels, contrary to what would appear from the present work, transformation in the pearlitic range is reasonably fast. The authors state briefly on p. 69 P of the paper that "insufficient information was available concerning the isothermal transformation characteristics of the steels employed, particularly for large specimens with large grain-size and a high hydrogen content." Thus they themselves realize that the transformation characteristics of the steels are profoundly modified by heating to the very high initial temperatures necessary to impregnate them with hydrogen, but they ignore this in the subsequent discussion. That is most unfortunate, because, if it had been taken into consideration it would have been found that most of the low-alloy steels referred to by them can be easily transformed in the pearlitic range.

In conclusion, I would suggest that the authors appear to have a fondness for the complex and a reluctance to accept the simpler straightforward practical conclusions of their own excellent work.

Mr. R. EBORALL (British Non-Ferrous Metals Research Association): I was very interested to see this paper, because I have recently been concerned, with Dr. Ransley, in some rather similar

work on an aluminium alloy.* I should like to congratulate the authors on the great progress which they have made in rationalizing this subject of hair-line cracking, and to refer to the sections of the paper dealing with isothermal removal, particularly with regard to austenite.

The authors give a semi-empirical formula for the amount extracted in a given time, and fit this

Fig. C shows all the experimental points of the authors for 1100° C., compared with the theoretical curve. The hydrogen content is expressed as a fraction of the original content. The agreement is fairly good, but after 5 hr. there is rather more hydrogen left than would be expected from the calculated curve, suggesting that a small residual amount, though not quite so large as that required

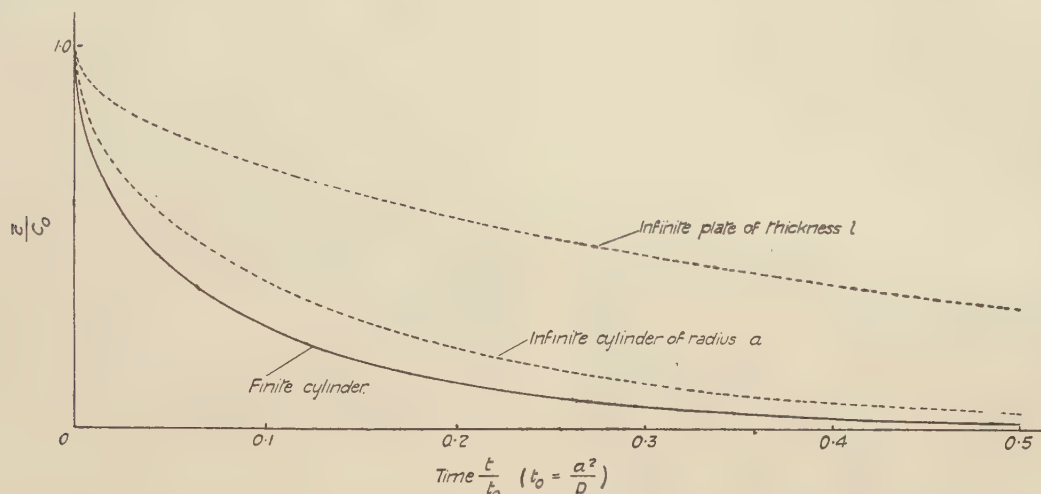


FIG. B.—Calculated Extraction Curve. Diffusion out of finite cylinder with $l/a = 16/7$ (l = length and a = radius).

to their experimental points by adjusting the time-scale and assuming a certain amount of hydrogen to remain unextracted after an infinite time. In our work we were faced with the same problem of diffusion out of a finite cylinder, and we were able without approximation to derive a suitable equation.† Fig. B shows the shape of the calculated curve for a cylinder of the proportions used by the authors. A curve for an infinite plate of the same thickness as the length of the cylinder, and one for an infinite cylinder of the same radius are given for comparison. It will be seen that at zero time the curves are all tangential to the concentration axis, and in fact they approximate closely to parabolae at the beginning. Departures from this form of curve are obtained (among other cases) where there is control by a slow surface reaction, in which case a simple exponential curve is obtained, or where the initial distribution of hydrogen in the metal is not uniform.

by the authors' expression, may remain in the steel after prolonged treatment.

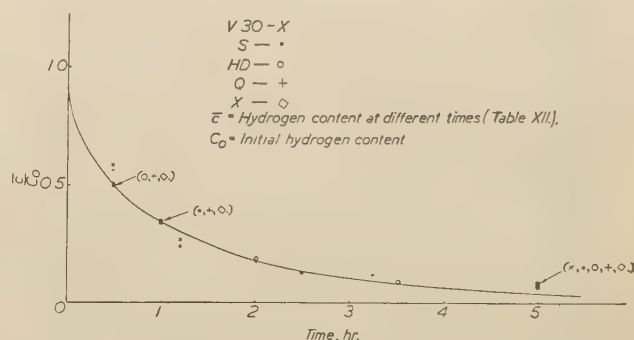


FIG. C.—Comparison of Authors' Experimental Points for 1100° C. with the Theoretical Curve.

At lower temperatures there was some loss of hydrogen before the first estimation was made,

* R. Eborall and C. E. Ransley, *Journal of the Institute of Metals*, 1945, vol. 71, p. 525.

† The appropriate form of the equation is :

$$\frac{\bar{C}}{C_0} = \left\{ 4 \sum \frac{1}{\beta_n^2} \cdot e^{-D\beta_n^2 t/a^2} \right\} \left\{ \frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{(2m-1)^2} \cdot e^{-D(2m-1)^2 \pi^2 t/l^2} \right\}$$

where \bar{C} = average concentration at time t ,

D = diffusivity,

l = length of cylinder, and

β_n = the n th root of the equation $J_0(x) = 0$, of which the first four roots are : $\beta_1 = 2.405$, $\beta_2 = 5.520$, $\beta_3 = 8.654$, and $\beta_4 = 11.79$.

C_0 = original concentration,
 a = radius of cylinder,

Further references and the conditions of validity of this equation are given in the paper referred to above.

owing to the time taken to transfer the specimens, and so forth, and this naturally affects the distribution of the gas in the specimen. Fig. D shows

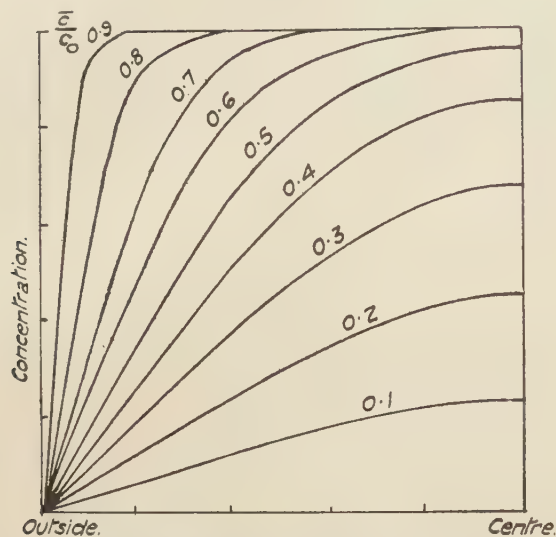


FIG. D.—Concentration Distribution at Various Stages of Extraction in an Infinite Cylinder (after Gurry *).

the distribution for an infinite cylinder at different stages of extraction. The curve is initially rectangular, and as time progresses it changes to a smooth curve of the type shown. Therefore, in applying the theoretical extraction curve it is necessary to start at a point on the curve corresponding to the fraction of hydrogen already lost. In Fig. E this has been done for the experimental points at 850° C. for steel *HD*. The time constant has been chosen so that the calculated curve fits over the first part of the extraction, and there is much more hydrogen left at the end than there

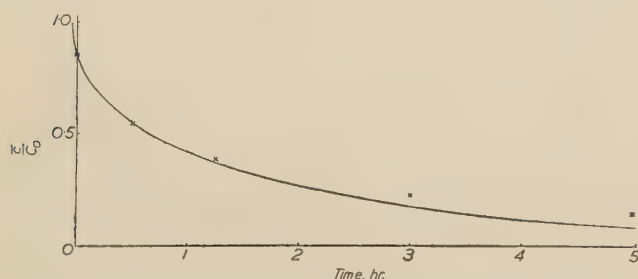


FIG. E.—Steel *HD* at 850° C. Initial content $C_0 = 7.70$ c.c./100 g. (from Table XII., 1100° C.). Hydrogen contents at different times (\bar{c}) from Table XII.

should be. In Fig. F it has been assumed that there is a limiting quantity of 0.80 c.c./100 g., and the agreement is now good. There is one thing wrong, however, and that is that the time zero of the calculated curve is not at -10 min. The authors' procedure was to make the first hydrogen determination on a specimen which had been in

the isothermal bath or furnace for 10 min., and to take the time of quenching that specimen as the time zero. One would therefore expect the calculated curve when fitted to have its zero at -10 min. (or at rather more, since for some of this time the temperature has been higher), but this does not appear to be the case here; it is in fact at -2.4 min. In other words, the quantity of hydrogen lost during the initial period was smaller than would be expected from the calculation. This may be due to a certain amount of restriction by a slow reaction at the surface.

At lower temperatures still, as in Figs. 20 and 21, the theoretical curve does not appear to fit, and the authors' simple exponential expression fits relatively well. This suggests that there is a still greater measure of surface control at these temperatures. The results below the transformation point, given in Figs. 25, 26, 27, and 29, are a good deal more difficult to deal with, as there is more than one phase present. Presumably there is a certain amount of austenite retained at the end of the experiment, which, on the authors' data, would retain some hydrogen.

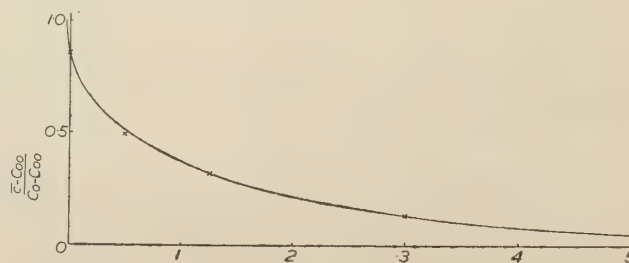


FIG. F.—Steel *HD* at 850° C. $C_0 = 7.70$ c.c./100 g., $C_\infty = 0.80$ c.c./100 g. ("limiting value").

I should like to raise a practical point with regard to the use of a salt or lead bath in this work. One would expect the hydrogen to come off as bubbles at the surface of the specimen, which would result in a back pressure of 1 atm. In this case the residual hydrogen at infinite time would be equal to the solubility at atmospheric pressure. Is this the case, or is there in addition diffusion through the bath?

Mr. R. WHITFIELD (Incandescent Heat Co., Ltd.): I should like to ask the authors whether there is any difference in dealing with steel with a hydrogen content in the case of an ingot which has been through a soaking pit and one which has been allowed to cool normally. I raise that point because of an experience some years ago on the Continent before the hydrogen content was seriously thought about. This was in connection with the manufacture of armaments and we started off with chromium-vanadium and chromium-

* R. W. Gurry, *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1942, vol. 150, p. 172.

molybdenum ingots of 70, 80, and 90 tons/sq. in. I was not so well versed in theory as Dr. Delbar, with whom I worked, and who was familiar with all these difficulties, and he was certain that gases played a very large part in causing the cracks. A tremendous amount of money had been spent on machining these ingots, only to discover hair cracks. I had a modest part to play in the work, and we came to the conclusion that gases did play a very important part. What it was, was then unknown, and the present paper is a step towards a solution of the difficulty.

Dr. Delbar had the view that it took time for the gases to come from the inside to the outside, and that if we exceeded a natural rate of extraction we should tend to seal up the outside against the inside and create a tremendous pressure which would start the hair cracks. I am using an analogy which may not be quite true, but which will illustrate what I am trying to say. In drying refractories there is a definite rate of drying, and if that rate of drying is exceeded, which is dependent on the capillary action of the movement of the moisture from the inside to the outside, it will be found over and over again that cracks are caused through sealing. Is that a feature in this case?

In the works in question, the ingots were made from basic open-hearth steel, and were then left to cool in the ordinary way, but the ingot was kept within the mould until it was reasonably cold and well below any possible critical change, as we then thought. The ingots were then drawn out and left to weather, and after allowing a period of time for this, were heated in a big, rather crude furnace. We decided that part of the cause of the trouble was the uneven heating in this old-fashioned furnace; there were temperature gradients all over the furnace, of the order of $\pm 100^{\circ}\text{C.}$, or 200°C. We therefore decided to build a new furnace in which there would be a proper control of temperature and uniformity all over the furnace. That furnace was built, and each of those ingots was put in and gradually brought up to 950°C. and kept there.

The point that I want to make is that Dr. Delbar, with his greater knowledge, told me that he did not want that furnace to go up at too great a rate, and so he obtained a chart of the furnace and ingot temperatures. There was a lag until the temperatures came together at approximately 950°C. , and then I had to keep them there for 2, 3, or 4 hr., but every run took at least 72 hr. We had two thermocouples actually on the ingot, in blocks, and four within the furnace, and they all had to be within $\pm 20^{\circ}\text{C.}$ They now run regularly, and easily, within $\pm 5^{\circ}\text{C.}$ The point is that, so far as I know—and I have been there many times since—hair-line cracks completely disappeared.

Mr. L. E. BENSON (Metropolitan-Vickers Electrical Co., Ltd.): While endorsing all that has been said of the great value of this paper, I want to say a word in criticism of conclusion (iii) on the last page of the paper. I have been unable to find sufficient support for it in the paper itself. Conclusion (iii) states that "Hair-line cracks may occur in the absence of transformation stresses," and, like Dr. Sykes, I think that this conclusion is a little unfortunate.

It seems to me that whether local transformation stresses high enough to cause cracking will occur or not depends on three things, all of which would need serious consideration before such a sweeping statement as conclusion (iii) could be made. One consideration is the speed at which the transformation occurs, bearing in mind that if a stress builds up as the transformation proceeds it will at the same time be tending to be relieved by a process of rapid creep. The rate of the transformation is very important, therefore, in determining how far stress-relief effects have to be taken into account.

The second consideration is the way in which the transforming spreads through the section, either from a number of centres or from the middle outwards, or according to some other pattern, because what is going to determine whether a crack occurs is the local stress. Here one has to bear in mind the effect of both major and minor segregation effects which may introduce further complications.

Thirdly, there is the question of whether stresses due to local transformation effects are superimposed on top of another stress system merely through rapid heating or cooling. I think the authors must agree that a great deal of work remains to be done before we have even an approximate picture of how the above conditions operate. I regret conclusion (iii) because I fear that it may mislead people who read the paper and who are not completely conversant with the whole of this exceedingly complicated question.

Dr. J. H. WHITELEY (Consett Iron Co., Ltd., Consett): It will be agreed, I am sure, that this paper records an excellent piece of painstaking work on the effect of hydrogen in steel. But that hair-line cracks are due primarily to hydrogen I cannot as yet accept without reservation. I prefer to keep an open mind on the matter. The results given in Table XXVIII. certainly appear to warrant that attitude, since out of the eight samples investigated in the isothermal tests no fewer than five are stated to be anomalous. Now, that is a curious state of affairs from the hydrogen-theory point of view for it is only on the fixed belief that hair-line cracks are mainly caused by hydrogen that the first three steels can be said to be not anomalous. I think the authors will admit that

five anomalous samples out of eight is not very strong evidence for the theory.

I was particularly interested in the anomalous and presumably acid steel, *K6*, since it has practically the same analysis as British steel rails in which hair-line cracks sometimes occur. In the trade these cracks are often termed grey spots, as they have that appearance in the fracture. That they are genuine hair-line cracks there can be little doubt, for they are of random distribution well within the rail head and can be detected in planed sections both by deep-etching and by the magnetic method. The defect seems to be confined to basic-steel rails, particularly when sorbitized, although I understand that it is not encountered by every maker. Apparently the cracks are formed at some temperature between 550° C. and 200° C., since they can be eliminated by a retarded cooling in which their temperature drops through that range in 35–40 min. Now, the authors have quenched samples of *K6* at various temperatures in the same range, and also below it, without producing any cracks, and I am confident that if it were possible to make comparable tests by taking samples from a rail immediately after sorbitizing, without further cooling, many cracks would occur, provided, of course, that the rail was one which gave hair-line cracks when cooled on the mill floor. This seems to be a case where experimental evidence and results in practice do not agree, and it makes one wonder whether, if hydrogen is the real cause of cracking, it has the same effect when introduced at 1100° C. as when present in the steel on casting. I admit that a weak point in this comparison is that I cannot give the hydrogen content of rails which show hair-line cracks but, judging by the results so far obtained on basic steels, it seems scarcely likely to have been much, if at all, higher than 7.0 c.c./100 g., an amount which the authors obtained in one of the samples of *K6*.

That there is a considerable amount of evidence in favour of the hydrogen theory is undeniable. The fact that samples heated in nitrogen do not give cracks when quenched is, I think, the strongest point of all; indeed, it seems almost a conclusive proof. Yet it is possible that samples heated in hydrogen are not exactly comparable with those heated in nitrogen. For instance, does the presence of hydrogen in the steel increase the heat conductivity so that quenching becomes more drastic as the amount of that element rises? Then, too, one might inquire whether the nitrogen contents of the samples are the same after they have been heated for 24 hr. at 1100° C. in hydrogen and nitrogen respectively. If so, is the distribution of the nitrogen the same in both cases?

Dr. R. J. SARJANT (Messrs. Hadfields, Ltd.): I should like to raise a few points on the question of

the reheating experiments described in certain parts of the paper. The authors have given, in their experiments on the removal of hydrogen, a number of ranges of temperature of hydrogen extraction which were to me somewhat surprising, but they are a fact, of course, and we must recognize them. In view, however, of the satisfactory results obtained by treatments at higher temperatures, one would hesitate to attempt to change to the treatments as low as are consistent with the authors' optimum temperature for the removal of hydrogen.

We carried out some reheating experiments on 3-in. and 3½-in. sq. billets, using steel *DA*, the manganese-molybdenum steel, which we were also treating isothermally. At 475° C. we tried giving the steel 12 hr., and even then the flaws were not eliminated; yet this is the temperature range given by the authors which is the optimum for the removal of hydrogen from that particular steel, or rather, for steel of a similar composition, namely, *FA*. On the other hand, by cooling and reheating, all the flaws were eliminated in 3 hr., whether the temperature used was 500° C., 650° C., or 680° C., and flaws were eliminated at 650° C. by soaking for 1 hr. only. Obviously, therefore, the treatments which are applied on rolled billets under works conditions, and those described by the authors are not comparable. I agree with previous speakers that the incidence of quenching and the small size of the test-piece have altered the matter.

In the reheating experiments described on p. 93 P and which were reported to the Committee by Mr. Dawson, the technique was to take a rolled billet from the mill, reheat and soak for the specified period, and then air-cool. From the test billets used in those experiments, specimens were prepared for the authors' experiments and the results of these are reported in Tables XIX. and XX. The object was to compare the behaviour of the small hydrogen-soaked specimens with that of the billets in regard to the removal of cracks. The steels tested were *DA*, *DB*, and *DC*, and in each case we found that cooling and reheating completely eliminated the cracks, whereas the authors were not able to repeat that in their experiments. On the other hand, reference to Table XX. will show that in only one specimen, *DC1* were the cracks eliminated by the authors by their technique, which of course was the technique of water-quenching of hydrogen-soaked specimens followed by reheating to 650° C., soaking for 2 hr., and brine-quenching. It is interesting to note from Table XXII. that no cracks occurred on quenching steel *N17* from 650° C., where there was a hydrogen content of 3.66 c.c./100 g. That was following the very rapid heating employed. Cracks occurred in a similar steel with slower heating, and it may be

that quenching into the lead bath, followed by the usual soak and afterwards water-quenching, may give results more in line with those we found in the works.

It would be interesting to know how the particular technique which I have just mentioned, and which the authors used, would work out on the steels reported on in Tables XX. and XXI. They contained cracks after treatment, and it would be interesting to know whether this modified method would remove the cracks, having regard to the fact that quenching or cooling conditions may produce them.

Incidentally—this has no bearing on the fundamental question, but is more or less an incidental piece of information of interest—we noticed that in determining the hydrogen content of the steels from the ladle, using the method of casting the steel direct into a water-cooled mould, the small chill-cast ingots, being about 1½-in. in dia.

comparison between the hydrogen removed by reheating and soaking at 650° C. for 2 hr., and that removed by isothermal treatment at the optimum temperature for 5 hr. The comparison is possible for three steels only, but Table B shows that in each case the reheating treatment gave considerably lower final hydrogen contents and higher percentages of hydrogen removed.

The question thus arises of whether the hydrogen present is the cause of cracking, and, if it is, why do the reheated steels give cracks in these experiments, whereas the isothermally treated steels do not? In our experiments we found it the other way round; we got cracks in the isothermally treated steels but not with the reheating treatment.

I was interested to hear Mr. Burton say that he was doing experiments with cooling down and reheating; we are working on similar lines. I think that these experiments are going to have some interesting results. The chief significance of

TABLE B.—*Comparison of Hydrogen Removal by Optimum Isothermal Treatment and by Reheating Treatment.*

Steel.	Type.	Optimum Isothermal Treatment (5 hr.).				Reheating Treatment (2-hr. soak) (Table XXI.),		
		Table.	Initial H ₂ .	Final H ₂ .	H ₂ Removed, %.	Initial H ₂ .	Final H ₂ .	H ₂ Removed, %.
4S11	3½% Ni-Cr-Mo	II.	4.67	0.59	87.4	6.53	0.43	93.4
FA	1½% Mn-Mo	IV.	6.31	0.38	94.0	6.45	0.28	95.6
CM	3% Cr-Mo	VI.	{ 6.72 4.63	{ 0.9 * 1.06 †	{ 86.6 77.1	9.58	0.75	92.2

* High-temperature range.

† Low-temperature range.

and 3-in. long, were found to contain cracks when they were sectioned and etched. They were only radial cracks, and we could not find any deep-seated random cracks. We put them down simply as stress cracks, that is, cracks due to rapid cooling; they did not occur with air-cooling of the specimen, and they had absolutely no correlation with the susceptibility of the steel, as determined by taking an air-cooled billet from the mill and testing it by supersonic examination. This latter is a sound method of determining whether a steel is susceptible or not.

The most significant feature of the experiments described by the authors is the low hydrogen content found in all cases after reheating. It is possible from the figures given in Table XXI. and in Tables II., IV., and VI., to draw up a

the transformation appears to be in regard to the differing solubility in the α and γ conditions. We have worked on the principle of getting well under the change point to get the steel first in the α condition, and then, before the expiration of the incubation period, reheating up to the point at which there is the maximum degree of diffusion of hydrogen, but I shall not be surprised to find that if we go above that temperature in the reheating treatment we may still get some improvement. There is something happening in addition to the effect of hydrogen and the straightforward transformation stress. I agree with other speakers that the transformation stress has something to do with the problem, but I still believe that there is a third factor operating of which we have no knowledge as yet.

CORRESPONDENCE.

Mr. A. G. HOCK (Workington Iron and Steel Company) wrote: The writer wishes to express his admiration for this remarkably good paper.

Close reading of the experimental results and of the reasoning which inspires these experiments

yields the realization that the results obtained are applicable fairly easily to practical cases, except perhaps for very large masses. For this latter case the writer's experience is limited.

It is satisfying to gather that the diffusion

constant does not vary appreciably for all austenites, even when one-quarter of the iron is replaced by nickel. Figs. 23 and 24, which can be re-plotted on a D basis, form a most valuable condensation of data for this state.

It is an excellent feature of this paper that it has shed much light on this subject and has posed a number of new problems for elucidation. It would be interesting to learn if the authors have performed their experiments on austenitic manganese steel.

Information upon the original hydrogen content of the samples used for experiment would be an interesting addition to the paper. This information could be considered in connection with the existence of a limiting concentration of hydrogen during evolution, especially if some knowledge of previous history could be made available.

The way in which the authors have used solutions of the concentration equation applicable to an infinite slab and an infinite cylinder is ingenious and worthy of the utmost praise. It typifies the way in which progress has so often been made, and, with the slightest care, the magnitude of the error involved can be realized fairly accurately.

The reference on p. 82 P to Barrer's "Diffusion in and through Solids" stated that a general solution of the problem of loss of hydrogen from a cylinder of finite length cannot be given. This aroused scepticism because of the belief that the problem of the finite cylinder in potential has been solved for all initial and boundary conditions likely to be met in practice and expressible in analytic functions of relative simplicity.

These conditions are simple in the problem which arises in the authors' work and a solution for the finite cylinder has been run out fairly easily.

An outline, using only elementary processes, can be given with some use of symbols and the tacit implication that all the transformations are justifiable.

If the initial concentration is c throughout the cylinder, and c_0 at the free surface during the diffusion, and if Laplace's operator be denoted by ∇ , then c is the appropriate solution of $\delta c / \delta t = a^2 \nabla^2 c$, when a^2 is a diffusion constant and t denotes time.

It is convenient to transform Cartesian to cylindrical co-ordinates, r, θ, z , in which the cylinder represents the space :

$$0 < r < \rho; 0 < \theta < 2\pi; -l < z < l.$$

The identity

$$dc = \frac{\delta c}{\delta x} \cdot dx + \frac{\delta c}{\delta y} \cdot dy + \frac{\delta c}{\delta z} \cdot dz$$

determines

$$\begin{aligned} \frac{\delta}{\delta x} &= \cos \theta \frac{\delta}{\delta r} - \frac{1}{r} \sin \theta \frac{\delta}{\delta \theta} \\ \frac{\delta}{\delta y} &= \sin \theta \frac{\delta}{\delta r} + \frac{1}{r} \cos \theta \frac{\delta}{\delta \theta}. \end{aligned}$$

Change the variable to

$$u = \frac{c - c_0}{c_1 - c_0}.$$

The transformed equation

$$\frac{\delta u}{\delta t} = a^2 \nabla^2 u$$

will be seen to break up into the form $u = RTZ$, when capitals represent functions of one variable only. Collecting terms yields :

$$\frac{T'}{T} = -\alpha; \frac{Z''}{Z} = -\beta^2; R'' + \frac{1}{r}R' + \lambda^2 R = 0,$$

provided that $\alpha = a^2(\lambda^2 + \beta^2)$; u is to be restricted to unity when t is zero, to zero when $r = \rho$ and when $z = \pm l$ for all values of t .

Appropriate solutions for T and Z are negative exponentials and circular functions respectively and that for R , with no infinity at $r = 0$, can be taken as :

$$J_0(\lambda r) = \frac{\sum_0^{\infty} (-1)^r \cdot \left(\frac{\lambda r}{2}\right)^{2r}}{[r] [r]}.$$

The boundary conditions require that the following be satisfied :

$$\sum_{\sin}^{\cos} \beta z \cdot J_0(\lambda r) = 1 \quad . \quad . \quad . \quad (1)$$

for all values of z and r when $t = 0$

$$J_0(\lambda \rho) = 0 \quad . \quad . \quad . \quad . \quad (2)$$

$$\sum_{\sin}^{\cos} (\pm \beta l) = 0 \quad . \quad . \quad . \quad . \quad (3)$$

The last two relations define λ and β . Assume the expansion of unity in a Fourier sine series of integral multipliers of :

$$\frac{\pi}{2l}(z + l)$$

and also in a series of Bessel coefficients of "zeroth" order in r , in the successive roots of $J_0(\lambda \rho) = 0$. Determine the coefficients of such expansions by reference to the equations satisfied by Z and R and the solution is :

$$u = \left[\sum_1 p_n \sin \frac{n\pi}{2l}(z + l) e^{-\frac{a^2 n^2 \pi^2 t}{4l^2}} \right] \left[\sum_1 q_n J_0(\lambda_n r) e^{-a^2 \lambda_n^2 t} \right].$$

It is readily verifiable that the solution satisfies the boundary conditions. p_n is given by :

$$p_n \int_{-l}^l \sin^2 \frac{n\pi}{2l}(z + l) dz = \int_{-l}^l \sin \frac{n\pi}{2l}(z + l) dz,$$

which excludes even values of n and gives the general term :

$$P_{2n-1} = \frac{4}{(2n-1)\pi}.$$

q_n is determined by :

$$q_n \int_0^l r \cdot [J_0(\lambda_n r)]^2 dr = \int_0^l r \cdot J_0(\lambda_n r) dr,$$

-because

$$\int_0^l r \cdot J_0(\lambda_n r) J_0(\lambda_m r) dr = 0,$$

which occurs on account of the relation :

$$J_0(\lambda_n \rho) = J_0(\lambda_m \rho) = 0.$$

Hence

$$q_n \cdot \frac{\rho^2}{2} [J_0'(\lambda_n \rho)]^2 = -\frac{1}{\lambda_n} \cdot \rho \cdot J_0'(\lambda_n \rho)$$

$$q_n = \frac{2}{\lambda_n \rho} \cdot \frac{1}{J_1(\lambda_n \rho)}$$

since

$$J_1(\lambda_n \rho) = \sum_0^{\infty} \frac{(-1)^r \left(\frac{\lambda \rho}{2}\right)^{2r+1}}{r! (r+1)!}.$$

With these values of p_n and q_n the solution for c becomes :

$$c = c_0 + \frac{8}{\pi l} \cdot (c_1 - c_0) \left[\Sigma_1 \frac{1}{(2n-1)} \sin \frac{(2n-1)\pi}{2l} \cdot (z+l) e^{-\frac{(2n-1)^2 a^2 \pi^2 t}{4l^2}} \right. \\ \left. \left[\Sigma_1 \frac{J_0(\lambda_n r) e^{-a^2 \lambda_n^2 t}}{\lambda_n \cdot J_1(\lambda_n \rho)} \right] \right].$$

The concentrations determined in the experiments are the integrals per unit volume :

$$c_m = \frac{1}{2\pi \rho^2 l} \int_0^{\rho} \int_{-l}^l \int_0^{2\pi} c \cdot r dr \cdot d\theta z = c_0 + \frac{32}{\pi l^2} (c_1 - c_0) \\ \left[\Sigma_1 \frac{1}{(2n-1)^2 \pi} e^{-\frac{(2n-1)^2 a^2 \pi^2 t}{4l^2}} \right] \left[\Sigma_1 \frac{1}{\lambda_n^2} \cdot e^{-a^2 \lambda_n^2 t} \right].$$

For values of t which are not very small, this reduces to :

$$c_m = c_0 + \frac{32}{\pi^2 \rho^2} \cdot (c_1 - c_0) \left[\frac{\rho^2}{(2 \cdot 405)^2} \right] \left[e^{-\frac{(2 \cdot 405)^2 a^2 t}{\rho^2}} - \frac{a^2 \pi^2 t}{4l^2} \right]$$

which is easily evaluated.

This can be arranged in the form :

$$\mu = \frac{K}{1+a} \cdot (1 + ab \cdot e^{-Nt})$$

for fitting to the authors' experimental curves.

It is useful to note the analogy between this result and the two other expressions used by the authors. As always, the judicious use of approximations involving purely unidirectional and radial flow has been justified.

The above outline of a correct solution for the finite cylinder must repeat, without doubt, a result known for possibly more than fifty years. It illustrates also two small errors in the arguments advanced by the authors on pp. 82 P and 83 P.

At the top right-hand of p. 82 P, the necessary integration has not been performed. Since differentiation of their expression is permissible (their expression is zero at the ends of the interval), it follows readily that the concentration given in the paper is not the average concentration but the maximum concentration at a particular time t . It should be noted that diffusion is indicated at both $x = 0$ and $x = L$.

The average concentration contains the factor 0.81 instead of 1.27.

On p. 83 P, argument is advanced for a value of b lying between 1.237 and 0.69. To the purely radial loss in a finite cylinder must be added the end losses, and it seems that the value of b must be less than 0.69 because their equation (10) shows that b varies in the same direction as the concentration of the remaining hydrogen.

The value obtained theoretically for the finite cylinder is $32/5 \cdot 8\pi^2$, or nearly 0.56.

To a sufficient degree of approximation the concentration can be modified to give an exponential after some little time.

Take :

$$\mu_m = \frac{c_m - c_0}{c_1 - c_0},$$

then the plot of $\log \mu_m$ is linear in t . This entails, however, the determination of c_0 in the experiment.

AUTHORS' REPLY.

The AUTHORS wrote in reply : We wish to thank all who have contributed to the discussion, but we are particularly grateful to Mr. Burton and the members of the Hair-Line Crack Sub-Committee, whose support and encouragement have made this work possible.

Mr. Burton's brief review of the earlier history of the Hair-Line Crack Sub-Committee is valuable. We agree with him that the divergent opinions amongst steelmakers in the past as to the best heat-treatment for the prevention of hair-line cracks are due mainly to the different sizes of the articles with which different firms have to deal, and to somewhat hasty comparisons being made without due consideration being given to variations in manufacturing procedures existing in the

different works. The paragraph quoted by Mr. Burton was intended to refer to the different opinions frequently expressed by steelmakers as to the order of susceptibility of different steels to hair-line cracks. We now realize that in making such comparisons the individual characteristics of the steel in response to heat-treatments should be considered, as well as the hydrogen content of the specimen. We are glad to have Mr. Burton's practical experience in this matter and we hope to deal with this particular point more specifically in a paper about to be published.

Mr. Burton and many other speakers raised the question of transformation stresses. There is no doubt that this question of stress is of extreme importance, particularly when dealing with large

steel forgings. In large masses it is very difficult to ensure uniform stress distribution, whether such stresses arise from transformation, cooling, or other sources, and it is true that in large masses the problem of hair-line cracks is more acute. It is in such large masses that hydrogen is usually present in quantities, however, and it is clear that, under industrial conditions, hydrogen and stress must coexist, and it is therefore not always easy to decide which factor is responsible for a given effect. Thus, we have, on the one hand, the fact that certain large forgings contain a considerable amount of hydrogen and at the same time are free from cracks, provided that certain suitable treatments have been given; this gives apparent support for the stress theory. On the other hand, we think we are justified, from both laboratory experiments and industrial results, in saying that hair-line cracks never occur in the entire absence of hydrogen. It may well be that in most practical cases both hydrogen and stress play almost equally important parts, and we agree, of course, that for a given hydrogen content hair-line cracks are much more likely to be formed in a steel which is already highly stressed.

The statement "hair-line cracks may occur in the absence of transformation stresses" was based upon what we consider an experimental fact. The specimens in question were those of 4S11, hydrogen-soaked, and isothermally treated at 330° C. for periods ranging from 25 to 90 min.; all the specimens showed random and deep-seated cracks. Micro-examination and hardness determinations carried out on these specimens indicated that their transformation was complete, and this conclusion was also supported by auxiliary dilatometric measurements carried out under similar conditions. With the size of specimen employed, we did not find it necessary deliberately to cool through a range of temperature in order to bring about complete transformation. It may be that the apparent conflict between Mr. Burton's experience and our results is caused by differences in the masses of steel involved.

Both Mr. Burton and Dr. Sykes have added to the "anomalies" listed in the paper by drawing upon their industrial experience. These facts could easily be interpreted as evidence against the hydrogen theory, and Dr. Whiteley has chosen to do so. We were very conscious that we could not explain these facts when the present paper was written, but work now in progress is throwing more light upon this aspect of the problem.

We are not altogether surprised at the tensile results given by Mr. Burton, in which a hydrogen content of the order of 5 c.c./100 g. did not cause any appreciable embrittlement of the material, because we have already found that with a 3% chromium steel, for example, and given a certain treatment, the test-piece may contain 3 c.c./100 g.

of hydrogen and show normal ductility. A similar hydrogen content causes marked embrittlement, however, if the steel is given a different thermal treatment. In this connection it is important to remember that all the tensile test results given in this paper were obtained on small specimens which had been air-cooled. We can definitely assure Mr. Burton that in all cases no surface cracking was observed.

We appreciate Mr. Burton's desire to see experiments carried out on large specimens; the lack of results on this side is due largely to the practical difficulty encountered in the handling of such specimens under laboratory conditions.

We are glad that Dr. Sykes was able to confirm the detrimental effect of hydrogen upon tensile properties of steel without having to introduce hydrogen into the specimen artificially. This confirms our view that the embrittling effect of hydrogen is of considerable industrial importance, although the effect is likely to be most pronounced when rapid cooling is effected. We are in complete agreement with Dr. Sykes' remarks upon the effect of hydrogen distribution across a cylindrical section, and we hope to show in our next paper that the tensile properties of a test-piece are definitely affected and varied with the manner in which hydrogen is distributed.

Although we are inclined to agree with Dr. Sykes that the diffusivity of hydrogen in carbon steels may be greater than in alloy steels, we wish to qualify the statement by saying that it may apply only to steels in the α state, especially at low temperatures. Thus we have results in hand, not yet reported, showing that the diffusivity of hydrogen at room temperature not only differs with different steels, but for a given steel it may vary with the treatment. Also, the solubility of hydrogen in a given steel at room temperature depends upon the transformation products present. These points are obviously very important, because the amount of hydrogen which a steel can tolerate will depend upon the solubility, and the hydrogen pressure that could be built up in cavities within a finite mass of steel would be governed by the rate of diffusion. The experimental method described in this paper for comparing the rate of hydrogen diffusion between different steels is admittedly not free from criticism, and was intended to give only a qualitative comparison of the different steels examined.

The importance of transformation products and the nature of transformation has been repeatedly stressed in our interim reports submitted to the Hair-Line Crack Sub-Committee, and we are extremely pleased that Dr. Allen agrees with us on this point. The demonstration of the effect of limiting value upon the hydrogen pressures which may be built up, as shown by Dr. Allen, is certainly instructive, and may help to explain

certain aspects of the hair-line-crack problem when more new facts are available.

In reply to Mr. Honeyman, the statement "in the austenitic range in all cases the number of cracks is, generally speaking, in agreement with the hydrogen content of the specimen," was intended to apply to the results on a given steel at a given temperature. It will be remembered that in the work referred to, five specimens were used for each temperature of isothermal treatment. It is quite obvious that results would not be comparable if specimens were quenched from different temperatures, because the stresses would not be the same. The comparison made in Mr. Honeyman's second point is not strictly a fair one, because the results given for hydrogen removal and those for isothermal transformation were obtained with different soaking periods. It is true that, according to Fig. 44 of the paper, transformation should not have commenced in 5 hr. at 550° C., but with shorter time of soaking and the larger specimens used for hydrogen removal, we have no evidence to show whether there was any transformation or not. On the question of complete transformation of 4S11 at a temperature of 250–375° C., we would refer Mr. Honeyman to the answer we have given to Mr. Burton.

We fail to understand Mr. Honeyman's assertion that we are "grudging in our admission" that transformation is accompanied by a rapid removal of hydrogen. In opening the discussion Mr. Burton pointed out that one of the outstanding features of the paper was the very clear demonstration of the relationship between transformation and hydrogen removal.

Mr. Honeyman quoted the figure of 2.08 c.c./100 g., which was given in Table IV. as the final hydrogen content of the manganese-molybdenum steel, *F*4, treated for 5 hr. at 550° C., and added that if the hydrogen content on reheating was given, a different picture would have been obtained. In general, when the hydrogen content of the specimen is low, say, 2 c.c./100 g., or less, no gas is evolved at room temperature, and the content given, therefore, was the actual hydrogen content of the specimen obtained on reheating only.

We definitely do not subscribe to the view expressed by Mr. Honeyman that most of the low-alloy steels employed in this work will transform readily in the pearlitic range; what of steels of the 3% nickel or the nickel-chromium-molybdenum type? We would agree that isothermal transformation in the pearlitic region is suitable for steels of the 1½% manganese-molybdenum or the 3% chromium-molybdenum type, but it is our opinion, and one which is shared by many others, that the treatment of cooling to 300° C. and reheating to 650° C. is of a much wider applicability to low-alloy steels in general.

We are pleased to have Mr. Eborall's contribution, drawing attention to the fact that solution for finite cylinders is available. It is gratifying to know that our "semi-empirical" equation led to conclusions similar to those which would have been drawn from the exact mathematical treatment. We have shown that the apparent limiting value of hydrogen content could not be explained on the basis of solubility, since the limiting value increased as the temperature and solubility decreased. Consequently, it would not be possible to explain this effect in terms of hydrogen bubbles at the surface of the specimen.

Mr. Whitfield's vivid description of his practical experience is interesting. It seems obvious that the rate of cooling affects the hydrogen diffusion and therefore the concentration gradient of hydrogen in a large ingot. As we have already pointed out, in dealing with large masses, thermal stresses due to uneven cooling or heating are important and should be taken into account together with hydrogen.

With regard to the point raised by Mr. Benson, our answer is the same as that given to Mr. Burton, *i.e.*, that conclusion (iii) was a statement of experimental facts. We appreciate Mr. Benson's remarks upon the importance of transformation and the speed and the manner in which it spreads through the section. Mr. Benson will see from our reply to Dr. Allen that we have for some time realized this although we put it in rather different words.

An answer to Dr. Whiteley's interpretation of the "anomalies" has been given in an earlier paragraph. We have no evidence to show that hydrogen increases the heat conductivity of steel; even if it does, we fail to see how this could cause cracks to be produced in hydrogen-soaked and not in nitrogen-soaked specimens. We have not determined the nitrogen content of these specimens by analytical methods, but microscopically no evidence could be found of nitride needles in nitrogen-soaked specimens. In industry, ingots are usually soaked at high temperatures in air, which contains some 80% of nitrogen, for longer periods than we soaked our specimens. Has Dr. Whiteley, in his long experience, observed any increase in the nitrogen content of low-alloy steel ingots after high-temperature soaking, as a general rule?

Dr. Sarjant's opening remarks imply that in works practice the removal of hydrogen from steel at high temperatures is not as efficient as our results suggest. This may well be true, but we think it can be explained by the facts that ingots or forgings dealt with in industry are heavily scaled, whereas in our experiments the removal of hydrogen was carried out with scale-free specimens and in a hydrogen-free atmosphere.

With regard to the differences shown by Mr.

Dawson's reheating experiments and our results, we agree with Dr. Sarjant that the failure to prevent cracks in certain steels by reheating, as shown in our paper, is probably due to the more drastic rate of cooling employed in our experiments. At the same time, we should like to draw attention to the fact that our specimen sizes are considerably smaller than Mr. Dawson's and that we have shown in an earlier paper that the smaller the specimen, the shorter the incubation period.

As already stated in a reply to Mr. Honeyman, we believe that cooling to a temperature at which the steel is completely transformed, followed by reheating to 650° C., is in general more efficient in removing hydrogen than is isothermal treatment, and this is supported by the comparison which Dr. Sarjant has made in Table B. Where we differ from Dr. Sarjant is that we do not believe that it is safe in all cases to cool the steel to room temperature before reheating, and our results show that, in certain cases at least, cracking results when this practice is followed. It appears that when this happens the cracks are formed either at room temperature or at an early stage in the reheating while the hydrogen content of the steel is still large. On the other hand, it will be remembered that in experiments on quenched specimens reported in an earlier paper, it was shown that crack formation was associated with a marked evolution of hydrogen from the specimen at a temperature which varied with the composition of the steel, and if, for example, the carbon content increased sufficiently, the marked evolution of hydrogen was delayed to such an elevated temperature that crack formation was not observed. It appears that a similar effect may have been operating in Dr. Sarjant's experiments and that, once allowance has been made for the difference in experimental conditions, particularly specimen size and rate of cooling, there is no real discrepancy between his results and our own. As far as the effect of isothermal treat-

ment is concerned, it should be remembered that cracking can occur only after cooling from the temperature of optimum isothermal treatment, and if Dr. Sarjant's treatment had removed less hydrogen than was the case in our experiments—and this seems to be quite likely in view of the important size effect—it would not be surprising if cracks were observed. This appears to be yet another case where an argument would be very much stronger if supported by reliable hydrogen determinations on the sample referred to, at the right stage in their history, and we would appeal for an extension of the use of critical hydrogen analyses in industrial practice as we feel sure that the final solution of the hair-line-crack problem would be greatly facilitated thereby.

Mr. Hock's demonstration of the solution of hydrogen diffusion in a finite cylinder in which an equation similar to ours has been derived, is most reassuring. We agree with him that the misinterpretation of the average concentration given on p. 82 P was caused by the slight error when the boundary conditions were assessed. We are conscious of the fact that, even with a linear gradient, the average concentration in the specimen does not necessarily correspond to $x = L/2$, but Mr. Hock will undoubtedly appreciate that by such an assumption, the solution given on p. 82 P is greatly simplified without affecting the form of the equation finally arrived at. We also agree with Mr. Hock that for a finite cylinder the end losses must be added to the radial loss, and therefore the value of b given in equation (10) may be smaller than 0.69.

We are greatly impressed by Mr. Hock's modesty in saying that our method of approach is to be recommended in preference to his mathematical treatment, and Mr. Hock's tributes to our work have been most kind.

We feel sure that Mr. Hock's attitude will greatly encourage those who undertake research problems necessitating a knowledge of higher mathematics to support experimental results.

Discussion on THE INFLUENCE OF PORT DESIGN ON OPEN-HEARTH FURNACE FLAMES.

The whole of the first day of the Autumn Meeting of The Iron and Steel Institute was devoted to a joint discussion based on the following two papers :

"The Influence of Port Design on Open-Hearth Furnace Flames." By J. H. CHESTERS and M. W. THRING (*The Iron and Steel Institute*, 1946, *Special Report No. 37*).

"A Heat-Flow Meter for Use in Furnaces." By R. H. BAULK and M. W. THRING (*Journal of The Iron and Steel Institute*, 1946, No. I., p. 41 p).

Dr. J. H. CHESTERS gave an introductory address on "The Purpose and Plan of the Experiments," based on Section I., Parts 1 and 2, and Section II., Part 8, of Special Report No. 37.

Three aspects were selected for verbal discussion, and these were discussed as follows :

Morning Session.

Special Instruments and Technique, based on :

Special Report No. 37 : Section I., Part 3, and Section II., Parts 1 to 7, 11, 13, and 14.

Paper by BAULK and THRING : Relevant sections.
Introduced by Dr. J. H. CHESTERS.

Afternoon Session.

Thermal Conditions within the Open-Hearth Furnace, based on :

Special Report No. 37 : Section II., Parts 10 to 14, and Section III., Part 2.

Introduced by Mr. M. W. THRING.

General Conclusions, based on :

Special Report No. 37 : Section II., Part 9, and Section III., Parts 1 and 2.

Mr. W. GEARY acted as rapporteur.

At a film display held in the evening of the first day of the Autumn Meeting a film entitled "Open-Hearth Furnace Flames," by Dr. J. H. CHESTERS, was shown. The film constituted a record of flame characteristics and other aspects of the trials and experiments conducted in the open-hearth melting shop at Templeborough.

PRESENTATION AND DISCUSSION.

THE PURPOSE AND PLAN OF THE EXPERIMENTS.*

Dr. J. H. CHESTERS (The United Steel Companies, Ltd., Stocksbridge, near Sheffield), presenting the report, said : The challenge responsible for the starting of the present work is shown as Fig. 1 in the Report. I have shown this illustration of the first furnace to be erected by Siemens at the Bay State Ironworks, South Boston, Mass., in 1869, to a large number of furnace designers and have asked them what they would think if I told them that we were proposing to install this small furnace as an experimental unit in one of our shops. Only one reacted immediately and violently, his comment being that there were no slag pockets. I suggest that if an automobile engineer was presented with a picture of one of the earliest motor-cars, he would have no hesitation in realizing that it was a "leg pull." There is no doubt that Siemens was well ahead of his time and that the furnace he evolved contained certain very sound ideas, but the fact that the furnace of

to-day is substantially similar was, we felt, a challenge to research work on this subject.

As a result of discussions between The United Steel Companies' Open-Hearth Advisory Committee and The British Coal Utilisation Research Association, it was agreed to carry out a rather extensive series of tests on three furnaces at Templeborough, representing roughly British, German, and American types of furnace. The criteria of performance chosen were output, fuel consumption, and refractories consumption. A team of some thirty-five men was got together and some forty-five records were kept of variations in gas flow, air flow, flame radiation, roof temperature, &c. There were many problems, such as the vast amount of water required for cooling probes, the complicated plumbing and wiring, and, last but not least, the synchronization of such a large number of readings. After nine months of planning, the work was begun and some fourteen casts were followed over a period of three months. A further three months' calculations and writing-up led to the present Report, which we would request you to consider as purely a preliminary

* A summary of the presentation.

skirmish, whose objective was merely to get "concepts" and some quantitative data that would aid the designer.

SPECIAL INSTRUMENTS AND TECHNIQUE.

Dr. CHESTERS (introducing this aspect of the discussion) said: The key instruments used were as follows:

"Internal" Instruments.

Heat-Flow Meter.—This has been described in the separate paper by Baulk and Thring. The fundamental idea is very simple. A calorimeter is exposed on one face to the furnace radiation, and the temperature rise of water passed through it at a constant velocity is determined. In the modified type, developed during the trials, two calorimeters were placed in series, one looking upwards and the other downwards. By means of such an instrument it is possible to determine, with a high degree of accuracy, the downward or upward radiation at any particular point in the furnace.

Front-Wall Pyrometer.—This is essentially a total-radiation roof pyrometer sighted through a hole in the front wall on to the flame. The results obtained are somewhat similar to those given by the heat-flow meter and there is more chance of such an apparatus finding day-to-day use.

Narrow-Angle Radiometer.—This consists essentially of two parts, a water-cooled target and a water-cooled probe, inside which is fitted a total-radiation unit. This latter can view part of the water-cooled target together with any flame that may be between the target and the end of the tube holding the radiation unit. If the flame were of extremely high emissivity, then the separation of the target and the tube would have no great effect, but if the flame is "thin," then the greater the thickness of flame the greater will be the reading on the radiation instrument. Use can therefore be made of this apparatus to get a rough estimate of emissivity.

Multiple Sampling Probe.—This is simply a water-cooled probe down through which pass four copper pipes emerging at four points along the side. By lowering it through a hole in the roof, samples can be taken simultaneously at four levels above the bath.

Cinematograph Camera.—Photographs taken through the doors, both perpendicularly and obliquely, enable the location, velocity, and stability of the flame to be determined. A new technique was devised in which strontium salts were introduced into the uptakes and photographed as they came through the furnace for determining the velocity.

Roof Pyrometer.—This was of the standard total-radiation type, being arranged to view the central portion of the roof through a hole in the back wall.

"External" Instruments.

Flow-Meters.—The problem of measuring dirty producer gas was overcome by building a refractory concrete "Venturi" throat in the vertical flue below the gas valve. This was kept clear by periodic blowing with a safe quantity of compressed air.

The air flow was measured by a mild-steel "Venturi" at the entry point.

Pressure Gauges.—Some sixteen pressure gauges were scattered over the whole system, the most important being the roof pressure, the stack draught, and the gas pressure behind each of the ports.

Suction Pyrometers.—Large suction pyrometers were built and were capable of being inserted into each of the six uptakes and run for considerable periods of time. Thus, in the last cast (H6) a practically complete record was obtained of the preheat and waste-gas temperatures for the whole of the cast period.

Waste-Gas Analysis.—A modified Mono apparatus was constructed to record both CO₂ and oxygen contents of the waste gases, and these were checked from time to time by means of Orsat equipment. The oxygen determination was made by passing the gases over carbon (after the initial CO₂ had been removed) and finding the amount of additional CO₂ formed due to the oxygen present.

Calorific Value of the Gas.—A Sigma apparatus fitted with suitable filters recorded the calorific value of the gas in the main. Samples were also taken for chemical analysis and subsequent calculation of calorific value.

Test Results.

The data obtained in the trials, which are summarized in the large charts contained in the Report, were supported by a great deal of statistical data obtained from normal practice. Certain of the main observations can be summarized as follows:

(1) There was a gain in output of about 2 hr. over the normal cast for the week, of which possibly as much as $\frac{3}{4}$ hr. can be attributed to the better scrap used. The remainder is considered to be the result of better combustion control made possible by full use of the information available.

(2) Fluctuations in downward heat flow, as shown by the heat-flow meters, were extraordinarily irregular. The variations have been analysed statistically in terms of the other variables recorded, and it is found that at the incoming end the gas volume explains little of the variation, but that the preheat changes explain about 70% of it. At the outgoing end, the gas-volume changes account for about 30% of the variation, but the preheat makes remark-

ably little difference, presumably because the higher preheat leads to a higher general temperature but a shorter flame. If the results are integrated over the bath surface and the typical downward-heat-flow figure is compared with the melting rate for the furnace, an essentially straight-line relation is found to exist.

Certain of the more important conclusions can be summarized as follows :

(1) Every furnace should be fitted with minimum instrumentation. This would include, in addition to fuel and air flow, roof-pressure and roof-temperature recorders and some means of following checker performance. A flame-power meter is also badly needed, though this is still in the development stage.

(2) There is still room for improvement in port design, the semi "Venturi" type having given the best results in the present trial. Certain modifications are suggested, but these will require to be tested out on models before large-scale furnaces are constructed.

(3) It is often found that after the furnace has recovered its roof temperature, following the completion of charging, a critical period sets in, in which the roof temperature can no longer be maintained, and the flame radiation as measured in the centre of the furnace tends to fall away. Since this occurs when gas flow, air flow, and calorific value are all reasonably constant, it is presumably due to the increased capacity of the charge to absorb heat. This suggests that additional heat should be available for this period, either in the form of a port capable of burning more gas, of carburetting, or possibly by the use of oxygen.

Dr. A. H. LECKIE (The British Iron and Steel Research Association) : I feel a little overwhelmed at being asked to open the discussion on this series of papers, which describe what must, I think we shall all agree, be the most stupendous piece of research ever undertaken on open-hearth furnaces in a works. I am also handicapped by having to follow Dr. Chesters, who has presented the subject so well and who has made things which have puzzled us for many years appear simple. Every contributor to the discussion will wish to pay tribute to the energy, ingenuity, and resourcefulness of Dr. Chesters, Mr. Thring, and all their colleagues in this investigation.

In view of the short time which we have had in which to study this Report, it is obviously difficult to discuss it adequately, and I must apologize in advance if I ask any question the answer to which is to be found somewhere in the Report, and which I have overlooked.

This morning we are discussing special instru-

ments and technique, and before going any further I should like to draw attention to one technique which Dr. Chesters did not mention specifically, but which I think is very important, and that is the very careful consideration given to the design of the experiments and the careful statistical study of the significance of the various figures. This is a very good example of the way in which a works scientific investigation should be carried out.

Statistical methods are still regarded by some as a new technique, though they have been used for many years in some industries. I would emphasize the necessity of using them in all investigations where the average of a number of widely varying individual figures is used for comparison purposes, as in the case of this series of tests. I wonder how many of us in the past have compared two averages of varying figures, one before and one after some alteration has been made, and claimed that the difference in the averages shows that there has been an improvement or otherwise. Without a test of significance, such conclusions may be false; if we take any two averages, even without making any alteration, they are likely to be different. This series of papers shows us how we should deal with such a problem, and shows the meticulous care necessary in determining the real significance of observations, which, indeed, is the only way in which the authors could have tackled this work.

Coming now to the special instruments and techniques used in these trials, we can divide these into two groups : (1) The improvement of methods of measurement which have been known for some time, and (2) the introduction of entirely new developments. In the first group we can include gas and air measurement, roof-pressure control, and roof-temperature control. The second group includes the heat-flow meter, the narrow-angle radiometer, the front-wall pyrometer, suction pyrometry in uptakes, and the recording of the calorific value of crude producer gas.

There is very little to discuss in connection with gas and air metering, because the methods have been known for a long time. Crude producer gas has been measured successfully in some works for many years, and where it has failed, the reasons set out on p. 35 are the cause—particularly low temperature at the metering point. There may be difficulties with old plants where the layout is bad; the Templeborough layout was particularly bad, and it is very creditable that it has been possible to carry out the measurement satisfactorily there. To say that it is not possible to measure crude producer gas in a new plant is entirely wrong, unless the plant has not been properly laid out.

I should like to ask whether it has been established that the Venturi is better than the snub-nosed brick orifice in all locations. It is better

in bad locations, but if you have a long straight main and the producer-gas pressure is adequate, is it better than the brick snub-nosed orifice?

I do not agree with the statement on p. 35 of the Report, that the use of Pitôt tubes is quite impracticable. In most layouts a Pitôt tube can be used for giving a rough idea of the flow in a spot test, though it is not suitable for continuous recording.

With regard to air measurement, the authors comment on p. 9 on the well-known fact that the meter gives only the air volume at the entry to the furnace and not at the ports. Do they agree that if the brickwork of the ingoing regenerators and uptakes is in good condition the infiltration is small? Some years ago we were rash enough to put a water-cooled Pitôt tube into the air uptakes, and we found that with good brickwork the volume at the port, or in the uptakes on the way to the port, was only about 5% more than was going in down below; and thus I think that it depends on the state of the brickwork. Mr. Halliday, on p. 61 of the report, refers to the calculation of air inleakage from CO_2 measurements in the downtakes, but he does not emphasize the fact that most of the infiltrated air in the downtakes at the outgoing end has come in through the doors and was not present at the air port. Some years ago Dr. Legg* did some measurements on direct infiltration, and reported 25% infiltration, which does not agree with our figure of 5%, but do the authors consider that with good brickwork—not plated, but maintained in good condition—infiltration at the ingoing end is not as much as we have been led to expect from CO_2 measurements in the downtakes?

The importance of roof pressure is demonstrated in this Report. The theoretical optimum roof pressure depends on the height of the roof, but for a furnace with a roof 8 ft. above sill level the optimum is about 0.1 in., and for a roof 6 ft. above sill level it is about 0.075 in. Do the authors agree with these calculated figures?

To show the importance of high pressure, and to confirm the findings in this Report, I should like to show the effect of roof pressure as measured on our experimental furnace at Shelton. From Fig. A the proportion of heat transferred to the hearth is seen to increase steadily until the optimum pressure is reached; that shows the advantage of running at high pressures. The actual pressure figures shown are applicable only to the small Shelton furnace and not to full-size furnaces where higher values are necessary.

I propose to say very little about roof-temperature control, because there are others here who can discuss that very much better than I can, and who know far more about it. I should like to ask, however, whether the authors are quite satisfied

that 1650° C. is the correct control temperature, because Shelton seemed to get away very well with, I think, 1680° C. If any of you still have any doubt about the value of roof pyrometry, you should go to see the furnaces at Shelton, where it has been used for years for process control and has given excellent results.

Dr. Chesters, in his introduction, referred to the difficulty of maintaining roof temperature after the required value has been reached soon after charging has been completed. I am wondering whether that is due to the time-lag in the appearance of the effect of the cold-charged materials on the checkers. I should think that with a large bulk of brickwork there would be quite a big

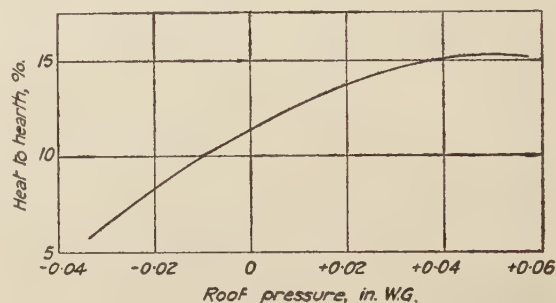


FIG. A.—Effect of Roof Pressure on Heat Transferred to the Hearth.

time-lag, possibly hours, before the checkers begin to feel the effect of the cold charge which has gone in previously. That may be one explanation of the fact that he got it up quickly to 1650° C. and had difficulty afterwards.

Coming now to the entirely new techniques, the most interesting is the use of the heat-flow meter in open-hearth furnaces. The extraordinary variability, almost from minute to minute, in the heat-flow-meter readings has been the subject of a good deal of statistical work by the authors. Brown and Fereday give one explanation for this variability; but I cannot help wondering whether other variables, such as rapid changes in air/gas ratio, not shown on the meters, and changes in furnace pressure, may not account for some of these variations as well as the preheat of the gas, and other matters discussed in the paper.

If, for instance, there is a 10-m.p.h. wind blowing into the furnace on the melting-shop stage, that is equivalent to 0.05 in. pressure, and if the roof pressure is not controlled automatically with a very rapid response mechanism, wind might cause considerable local changes in air infiltration which would affect flame temperature and, presumably, downward heat flow. Are the authors satisfied with their explanations of these rapid variations? For instance, changes in gas quality are blamed to some extent. I should like to ask

* *Journal of the Institute of Fuel*, 1932, vol. 6, p. 349.

the authors, therefore, whether similar changes in the heat-flow-meter readings were observed in their experiments at Appleby, where mixed gas of presumably constant quality was available.

The authors agree that the heat-flow meter is too cumbersome for routine work in melting shops, and it can be used only when the bath is flat. Although the heat-flow meter is not suitable for permanent fitting in a furnace, the front-wall pyrometer looks like becoming a simpler substitute.

While waiting for further information about the development of the front-wall pyrometer, I wonder whether such a device as the Mayorcas roof calorimeter, possibly built facing upwards into the table in front of the gas ports, would provide useful readings at the ingoing and outgoing ends. Although it would give only the extreme ingoing and outgoing figures, and also might soon become coated with slag, nevertheless its use might be worth considering.

It is a pity that the narrow-angle radiometer was developed so late in the trials, because more work with it should give very interesting results. We should like to see the effect of gas quality and of air/gas ratio on flame emissivity at or about the middle door. The middle door would be the best position, because there is a good representative section of the flame at that point. Flame spectroscopy is a subject which has not been much investigated, and although probably detailed study of the flame spectrum is not feasible because of the continuous background in the visible region, which is bound to be obtained with an open-hearth flame, if it were extended into the infra-red region, I think that some interesting results would be obtained, if it is possible to use rock salt or potassium bromide optical systems in a melting shop.

One of the measurements on which the authors are to be most congratulated is the continuous measurement of preheat by suction pyrometry. I know from personal experience the difficulty of suction pyrometry in a furnace uptake. One criticism of the pyrometer used in the present trials is that the radiation shield was not adequate for high-temperature work. Several concentric rings or a nest of small tubes, such as was used by Schack, are required. I realize that anything more complicated than the simple type which the authors used, might give endless trouble, but on p. 132 of the Report the pyrometer used is described as a Schack pyrometer, and I do not think that that is correct, because Schack's suction pyrometer, which was described in the Symposium arranged by the Institute of Fuel some years ago, consists of a nest of small tubes as a radiation shield, and is a very much more complicated piece of apparatus than can be used in an open-hearth furnace.

An interesting point about this preheat investigation is the remarkable similarity of air preheats that one gets in different furnaces. Fig. B shows some suction-pyrometer measurements taken some years ago in the uptakes of a 40-ton acid furnace at Monk Bridge. That is quite a different type of furnace from the one at Templeborough, but if the results are compared with those given in Fig. 43 of the Report the likeness will be seen. It is interesting to find that the average preheat temperatures and the difference between optical- and suction-pyrometer readings are very similar to those obtained on 80-ton basic furnaces. We found it difficult to keep the instrument in for more than 2 hr., and in the case of the one shown on the right-hand side of Fig. B, the shield began to fail after 1 hr. The present investigation shows, therefore, that the technique of suction

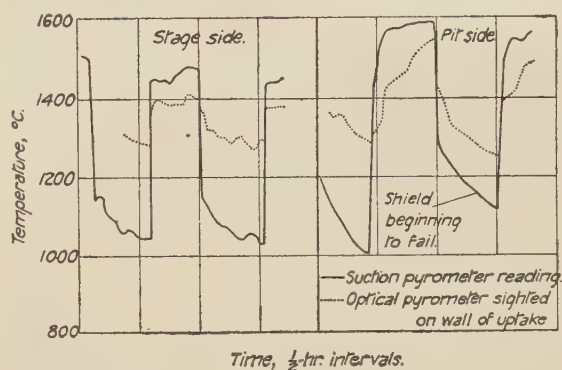


FIG. B.—Variation of Preheat Temperatures, measured by optical and suction pyrometers; 40-ton acid furnace at Monk Bridge.

pyrometry in uptakes has gone forward considerably, and that it can now be said to be quite practicable.

If you study the mean preheat temperatures quoted in the literature, and add 200° C. on to the preheat for optical readings (as has been suggested in the Report, and with which we agree) it will be found that most preheats in furnaces almost all over the world come to between 1100° C. and 1200° C., and that is irrespective, for instance, of different checker designs. At Monk Bridge, for example, the checkers were quite different from those at Templeborough, and so this suggestion of slag pockets and uptakes doing the major part of regeneration is confirmed. We are so confident that this factor is constant that, when designing a new furnace or in studying an existing furnace when there is no suction-pyrometer reading to guide us we assume a temperature of 1150° C. for the preheat and feel that we are not far out. The occasional readings of 1500° C. preheat noted by Dr. Chesters are, I think, time-lag from the waste-gas cycle, and not true preheat.

One question arises here which I should like to

put to the authors. There is an obvious explanation for the difference of 200°C . for the ingoing air between the wall temperature measured optically and the true air temperature measured by the suction pyrometer, *i.e.*, heat stored in the wall, but why is there such a very small difference on waste gas? I think Fig. 43 shows that the difference between optical and suction readings on the waste gas is only between 10°C . and 20°C ., while on the ingoing air there is this difference of 200°C . Would the authors agree that their work shows that the present practice of measuring pre-heat temperatures by radiation pyrometers sighted on top of the checkers should be replaced by the use of radiation pyrometers sighted on to the uptake walls? I think that even with the technique developed by The United Steel Companies we cannot yet say that suction pyrometers are suitable for continuous recording over really long periods, but surely the radiation pyrometers now found in many works on the top of the checkers should be transferred to the top of the uptakes, where they would give a very much better picture of the preheat than can be obtained with the checker pyrometers.

I have nothing to say on the recording of calorific value of producer gas or on the ingenious use of the Mono duplex recorder as an oxygen recorder, beyond congratulating those concerned on showing us how to do it.

I must comment, however, on Dr. Chesters' fascinating technique with the cinematograph camera. This may be a very valuable tool for the study of flames, but I am not clear how far it can be used to measure flame velocity as distinct from surge velocity. For a long time I have wondered whether we could measure flame velocities stroboscopically, but there is the difficulty of marking the flame at even intervals. The colour technique of Dr. Chesters should help in such a scheme, and the figures shown in Fig. 100 are most interesting. Those in the right-hand column, showing the incoming flame, are a remarkable illustration of the behaviour of a diffusion flame, and they should be compared with Fig. 1 of the paper by R. F. Davis,* which is included in the list of references on p. 16 of the Report. The spread of the turbulent mixing region is shown most clearly, and it helps to justify the use of the concepts summarized by Davis in open-hearth furnace flame investigations. I have tried working on Davis' arithmetic and the figures given by Dr. Chesters, and it is interesting to compare the flame velocities given by Dr. Chesters at the first and second doors with those calculated from equation (6) in the paper by Davis. In doing that it is necessary to assume a figure for Davis' jet characteristic; if that is taken to be 4.0—which is a little high, but there is no reason why it should not be for a port of that type—and

flame temperatures of 1700°C . at the first door and 1800°C . at the second (which seems justifiable, according to the figures of Mayorcas), the calculated velocity for an incoming velocity of 130 ft./sec. is 62 ft./sec. at the first door and 36 ft./sec. at the second door. That seems to show that Dr. Chesters' measurements do agree very closely with the mechanics of flame and air jets as given in Davis' extraordinarily interesting paper.

It would be interesting to calculate out the actual path of the flame by the combination of Davis' methods and the early Yesmann formula for the parabolic path of a flame.

I have not said anything about the water-cooled sampling-probe technique, because that speaks for itself, and is an obvious thing which everybody should do in making a serious investigation of open-hearth furnace flames. I do regret that the waste-gas volumes were not metered. It should be fairly simple to measure them by putting an orifice in the stack. One or two works do it, and experiments at Shelton show that the measurement of waste-gas volume is most informative and tells you a great deal about the behaviour of your furnace. However, to expect the authors to do that as well as all the other things would be "gilding the lily."

These trials have excited my admiration and envy during the whole of the time they have been carried out, and I think that many of us will be inspired to follow the example of Dr. Chesters and Mr. Thring and to carry out tests on similar lines in other works.

Mr. F. L. ROBERTSON (Messrs. John Summers & Sons, Ltd., Shotton): I wish to emphasize what an epoch in steelmaking these papers mark. We have here the results of fourteen charges run with measuring devices that would have been laughed out of court forty years ago. Of these we have three new graduates. The heat-flow meter, the front-wall pyrometer, and the suction pyrometer. All three have been on the verge of graduating for some time, but here for the first time we have them working over fourteen charges.

From absolute unmeasured chaos we have painfully come as far as this, and I think it were well that members took these papers as a landmark in our march toward precision. After all, the laws of chemistry are as precise as the laws of physics, and we are bound to hammer our liquid and gaseous metallurgical processes into as precise a job as the *Queen Elizabeth* or a modern rolling plant.

I had the privilege of seeing one of these fourteen charges through from the beginning and was thrilled to see in actual practice so advanced a stage of measuring the course of a charge. I congratulate those responsible and think it is from this platform the trade moves forward.

* R. F. Davies, *Proceedings of the Institution of Mechanical Engineers*, 1937, vol. 137, p. 11.

It is to this forward move—the using of the instruments—that I wish to confine my remarks. We form conclusions from instrument readings and then handle our furnaces so that the furnace makes the instruments give us the reading we think favourable for steelmaking. We then, surrounded by the enemy—uncontrolled variables—have to run hundreds, even thousands, of charges to consolidate our faith that the conclusions we chose as fundamental and the values we gave them were correct.

The fundamentals for precise melting that I chose for myself in early youth were gas quantity, highest furnace temperature, and high rate of heat transfer. It was round these as my headquarters that I set out to conquer each of the many interfering variables one by one.

The company I serve solved the fuel measurement, and furnace temperature measurements some eight years ago. With these as fundamentals and still waiting to bring heat transfer into the fold they have boldly advanced. Their faith that these are the fundamentals has been consolidated by thousands of charges, rising from 25%, 50%, 75%, up to 100% increased output.

It is therefore difficult for a steelmaker to view sympathetically conclusions about running charges drawn from the authors' gas-flow and roof-temperature charts. The gas flow and roof temperature are haphazard and follow no principle.

I suggest that the authors should have started by deducting and then empirically checking that each one of their furnaces could burn a given quantity of gas, the maximum, with the charge piled up to a given Plimsoll line. This quantity of gas should be supplied to the furnace as an absolute constant till the maximum roof temperature is reached. The roof temperature should now be kept constant by regulating the gas supply.

It is also difficult for steelmakers to view in any way deductions drawn from fourteen charges spread over three furnaces.

Would the authors not consider going into production, and with some fundamental principles such as I have mentioned seek to establish, by running some thousands of charges, rules of furnace design and process discipline.

With their beautiful instrument technique they would be assured of complete rout of the enemy—the uncontrolled variables.

Figs. C and D show the kind of curves that I think the authors' work should have been founded on, and on which I beg them to found a future work.

The *R* furnace is gas-fired and the charge is an ordinary production charge. The following points will be noticed from Fig. C :

(1) The gas flow up to 7 o'clock on each end is constant. The two ends differ by 15,000 although the gas screw has stayed put. Those

who use gas meters will recognize the trouble. At our present state of development we have to accept such a curve as a straight line.

(2) Up to 7 o'clock the roof temperature has never reached the limiting temperature (1640°C.) at which this furnace is to run. At 7 o'clock the

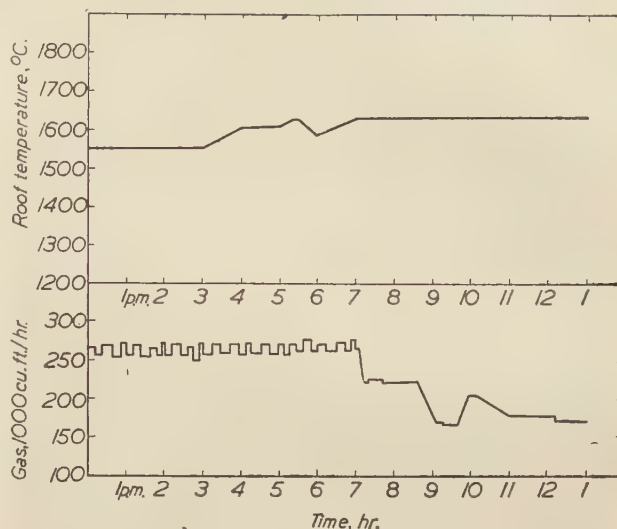


FIG. C.—*R* Furnace, gas-fired.

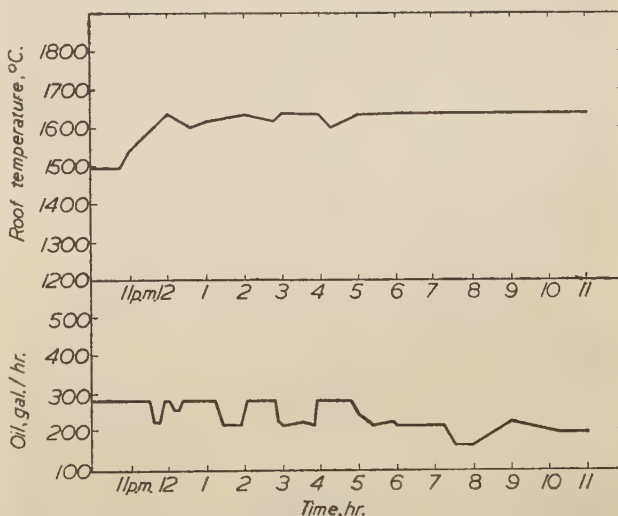


FIG. D.—*L* Furnace, oil-fired.

FIGS. C AND D.—Curves Showing Variation of Fuel Consumption and Roof Temperature throughout the Charge.

gas has to be cut down with characteristic suddenness to keep the roof temperature constant.

(3) The unevenness of the gas flow after 7 o'clock necessary to keep the roof temperature constant.

The *L* furnace is oil-fired, and from Fig. D it will be seen that :

(1) 280 gal./hr. is the maximum oil ordered for this furnace.

(2) In this charge, in contrast to the *R* furnace, the maximum or nearly the maximum roof temperature (1640° C.) has been reached during charging and the oil has had to be cut down. If the charge be examined carefully it will be seen that the operator has been just a little nervous and has erred with the oil screw a little on the safe side. It is, however, a good regulation.

(3) There is the same unevenness of fuel supply that we saw in the *R* furnace that is necessary to produce a straight line for the roof temperature, and the suddenness of the changes.

I would like to suggest that the authors, when they continue their work, pay close attention to changes of fuel supply under constant roof temperature. The matter is very closely tied up with slag weight and weight of lime necessary for a charge.

Lastly, I would like to refer to the authors' remarks on p. 161, section (a), where they claim that the use of instruments will increase the output by 10%. They are misleadingly modest. Instruments *qua* instruments will of course leave output unaffected. But if, as they obviously mean, instruments are used on a furnace as a means by which a melting-shop manager issues his orders and inspects how they have been carried out, then I boldly say that, with obedience to the authors' basic principles which I have culled from their Report, the output of most British furnaces will go up by 30–50%. My own firm has worked 50–70% increased output under less favourable conditions over long periods.

Let us consider the authors' principles :

- (1) Hearth area : 400 sq. ft.
- (2) Fuel supply until roof reaches 1650° C. : 350,000 cu. ft./hr.
- (3) Charge : 80 tons.
- (4) Constant roof temperature : 1650° C.
- (5) Slag weight : 8 tons.

When the authors return to their work of the influence of port design and start by a disciplinary devotion to their basic principles, they cannot help outstripping 50% increased output and probably change entirely the Siemens process as we know it.

Mr. H. C. ARMSTRONG (Messrs. Thos. Firth and John Brown, Ltd., Sheffield) : We must all agree with the eulogies of this work, and therefore I think that I may be allowed to pull Dr. Chesters' leg a little and tell him that I admire the naïve way in which he arrived at some of his conclusions, which of course he knew were there before he started. In our first early lectures in chemistry we were told that all combination must be between molecules, in other words, intimate mixing. I

have often thought, when looking at a furnace and seeing the gas and air coming in, that that word "mixing" has been an exaggeration; we have not had mixing. The effect of mixing and preheat on rate of heat release was pointed out a long time ago.

Another point which is not sufficiently brought out in the Report is the question of air/gas ratio. I think we are too apt to look upon the curve of rate of flame propagation with producer gas as a flat curve. With coke-oven gas with high hydrogen, a sharp peak is obtained, but the speed of combustion in a 1-in. tube for producer gas between the limits of 45% and 55% of gas in air, is given by Wheeler as varying from 2 to 2½ ft./sec. That is a 25% increase. I have been astounded in recent work which I have been doing with solid-coal/air ratio control to find what an enormous difference this air/fuel ratio does make. I think that eventually we shall get on to the Siemens fuel ratio control, which should give us a great deal. I suggest that that is probably responsible for some of the variations which are not quite explained.

Another factor which affects the temperature release is this question of roof pressure, which is coming very much to the fore now. I should like to call attention to something which is not mentioned in the Report : The influence of back pressure on the quantity of gas for air coming in. It is extraordinary what a large effect a slight alteration in pressure—probably something like 0.001 in.—will have on that. If you have studied the position in the old days with the steam-blown jet you will probably have noticed that a very slight difference in the back pressure made a great difference.

I am glad to see this question of pressure brought forward. I have calculated very roughly that it is possible to draw in some 44,400 cu. ft. of air per hour for every square foot of opening. That requires about 2,500,000 B.Th.U. to raise the temperature at which the furnace is working, but at an excessive pressure—about 0.07 or 0.08 in., certainly not more—you will find that it is possible to lose through heat coming out of the doors something like 1,000,000 B.Th.U./sq. ft./hr., so that this balance is a very tricky one. If you are going to talk in terms of positive readings on a pressure recorder, you must have a twin leg, because a single leg gives trouble through static head.

We did a good deal of work on similar lines to this many years ago, though with nothing like the same number of instruments, and our conclusions are almost the same. Reading through my conclusions, I think that where we disagree it is only because of our special conditions or because we were probably wrong. It is interesting that the work which we did before comes in in the same way. The air/fuel ratio comes in very well on

these curves and shows up very well, and the fact which is brought forward as a final conclusion, that the more gas that is put into a furnace the quicker it will melt, is shown up on my own curves, together with the fact that the thermal efficiency will drop when you are over-pushing the furnace.

It is suggested that the best furnace uses the most fuel. I do not think that it need dishearten us if we have to use more fuel to get a quicker melt, because we must go in for heat recovery by waste-heat boilers. Eventually we shall not be satisfied with any furnace as a furnace by itself; we must have regard to the heat-recovery plant throughout, and even if we have to put more heat through to get a quicker melt, I think that we can salve our conscience by picking it up later in the waste-heat boiler.

On the practical side, I should like to refer to the cleaning of the gas orifice by steam. We had to put all our orifices in horizontal flues. We used the round-nosed orifice, and our trouble was to keep the orifice clean, and it was difficult, if not impossible, to get a magnetic valve which would shut-off the steam tightly. We are now going to follow Dr. Chesters and try air. I would ask him who operates that air. It is all very well to have a B.Sc. to turn the tap on, but they are not there always. We had an arrangement worked from the meter clock, and every four hours the meter clock opened a relief valve. There is the danger that if it is done automatically in that way you may just catch the flow with very little gas in, and be worried about kicks.

The suggestion of having a CO₂ recorder on the producers is all very well, but there is a practical difficulty. I introduced it a good many years ago, because I wanted a scheme for paying a bonus to my gas-producer men, and I paid them a bonus on the CO₂, with a low limit. Our trouble, as has been shown in these tests, was to keep the filter clean, and I am wondering whether it is worth having a man to go round every day to change the filters every 24 hr.

I have read every word of this Report, which is a very good one, because it does show the furnace as a heat exchanger, and we have to look at it in that way. I think that it will take a good deal to make the steelmakers change their minds, but they will have to come to us on the fuel side and ask for help.

Speaking about our acid furnaces, where we take some awkward lumps, it may interest you to know that by selecting one or two charges and taking more convenient pieces and charging at a slower rate, our melting time was 34% better than the previous worst and 12% better than the previous best. We did all our experiments and plotting on melting time; we have kept away from the charging and we take the time from charge to melt. Almost the same result is obtained, but the important part is

the melting; so far as the charging is concerned, much as you would like to alter it, you have to take what is given to you. I suggest, therefore, that there is no need to include charging time in with melting.

I do not altogether like the mathematical method of getting out regression curves, but we are all guilty. They certainly give you a picture, but the spots fall so far apart from the curve that it is not possible to make much use of the curve as a control curve, which is what we want. As Mr. Robertson said, we want to control to previously known data, and if we can get clear curves we can stick to them, more or less.

A very interesting point which has come out of this investigation is that made by Dr. Chesters with regard to the checkers. That answers a doubt which was in my mind. If you remember the very fine Symposium which we had on steel melting in this Institute some years ago, you will remember that a very large number of figures were given, and the different volumes used for the checkers were astonishing. The volume varied greatly; one man obtained results with one volume per ton of steel and another obtained as good results with twice as much. I think that Dr. Chesters has found the solution, namely, that it is above the furnace stage level that everything happens, and that what happens below is of much less importance. That explains why it has been impossible for all these years to get any correlation between size of checkers and operation.

I should like to suggest to the authors that they should take the time of their gas in the furnace; I have found that a tremendous help. You have to give time for your producer gas to burn, usually about two seconds, but varying according to the port mixing. Where the fuel in the furnace is timed at below two seconds it will be very expensive on fuel, and if the time is much above that the furnace will be too sluggish. The time that the gas is in the furnace is of great importance, and it is worth watching.

Dr. J. H. CHESTERS: I should like to take this opportunity of thanking those who have spoken for the nice things they have said. We do quite sincerely consider this as a preliminary skirmish, even if with rather big battalions, and we know that some of our conclusions are decidedly uncertain. We had a good deal of searching of heart before we even put them down in writing, and we are quite prepared to alter them on any reasonable evidence. I am responsible, for example, for the figure of 1650° C. for roof temperature, because we found that the roof melted at 1680° C., which is apparently the temperature at which Mr. Robertson's roof also melts. The difference is that he thinks that he can keep his people in such good order, including

his instrument men, that he can rely on that figure of 1680° C. being maintained. We find that we are liable to have anything up to 30° C. of unexplainable error; one week it will be 20° low and a week later it will read correctly, without anything having been done to it. We are nervous, therefore, about pushing our figure up to 1680° C.

With regard to the idea of putting marks on the flames at intervals, which was raised by Dr. Leckie, we should be willing to do that and give him pulsations of strontium nitrate going into the uptakes at any frequency he likes, but whether the pulsations would come through into the furnace at the same frequency I do not know.

A major question is why we allowed our roof temperature to vary as it did, and why we did not avoid it by adjusting the gas. The answer is that we frequently did not have the desired amount of gas available. We had it on full unless we got to the stage where our roof looked dangerous. Long before we started these trials, the management at Templeborough were aware of this gas deficiency and had ordered new capacity, but we did not get it in time for these trials. If we had run Mr. Robertson's furnace, we should have kept his roof melting all the time!

Perhaps Mr. Brookes will reply to the question about orifice cleaning.

Mr. J. T. BROOKES: It is the responsibility of the Fuel Department. We have men working round the clock on instruments.

Dr. CHESTERS: Those are all the points that I want to mention at the moment, but Mr. Dall might tell us whether he thinks that the brick orifice is a good idea.

Mr. H. E. DALL (Messrs. George Kent, Ltd.): Part 2 of the Report deals with the difference between the characteristics of brick orifices and the Venturi tubes adopted for the test. Primarily the Venturi tube was chosen from considerations of pressure loss only, but perhaps it should be stressed that further advantages were revealed when model testing was carried out and still further when in actual operation. These further advantages operate even when pressure economy is not of prime importance.

The advantages consist in the greater stability of the coefficient with the Venturi tube, as compared with the snub-nosed brick orifice, not only with irregular locations, such as those at Templeborough, but also with straight-pipe locations.

From our experience with these and subsequent model tests, we have decided that Venturis are preferable to orifices for future use.

Square-edged thin-plate orifices in straight-pipe locations also give stable coefficients, but are liable to far greater errors if fouled with deposits of soot or dust.

The gas pressure at Templeborough furnaces was comparatively low, and it was feared that the melting time would be affected by the resistance of orifices. The Venturi tubes, given a differential of $\frac{1}{2}$ in. water-gauge, or so, at the top load, regain at least 80% of this, hence the quite negligible effect on the gas supply.

Mr. Armstrong referred to the question of operating the air blowing by automatic means. It is just as easy to operate with air as with steam; magnetic valves can be used and operated by contacts from the recorder just as easily, and in fact with greater reliability, because a magnetic valve will function more satisfactorily with compressed air than with steam.

Dr. P. M. MACNAIR (Messrs. Richard Thomas and Baldwins, Ltd.): There is one point in Dr. Chesters' remarks which I am not sure that I have understood correctly, and I should like to ask what his view is with regard to swirling. A number of years ago we thought that this idea of swirling was a good one, and the first suggestion was that we should swirl the gas in one direction and the air in the other direction, and that this would cause a great deal of confusion and so lead to better mixing. I would suggest to the authors that gas and air both ought to swirl in the same direction in order to avoid neutralizing the effect. In our experience with pulverized coal, we found that it was better to swirl them both in the same direction rather than in opposite directions, as it was understood Dr. Chesters had suggested with gas and air.

Dr. J. H. CHESTERS: In reply to Dr. Macnair, we were referring only to a model of a swirling burner. We have in our laboratory, and have had for a long time, a little furnace in which we can melt pure sand, forming a pool of glass. It is only a cubic foot in capacity and has two burners, one on each side, which oppose one another, thus increasing the rate of mixing. The waste gases go out at the bottom. Both the air and gas are preheated. There is one spiral which makes the gas spin one way, and another in the burner which makes the air spin the other way.

In Germany a burner was produced which had a sillimanite cup and use was made of the opposition swirling of two streams to get rapid mixing. This burner could be turned up from being like a candle to like a blow-torch, with a very short flame. The cup reaches a temperature of about 1800° C., and huge quantities of gas can be burnt in a small space. Some of the latest American strip reheating furnaces have a series of such burners, and when making tubes the steel is shot through at a high speed, the radiation being so enormous that the strip comes out sufficiently hot to roll.

We feel that if we could have something similar on an open-hearth furnace we should have only one new problem, *viz.*, the combustion would be so rapid and the flame so short that in the ordinary way the roof would melt. Whether, if we had first-class control and could pull out the "corkscrews" at the critical moment, we could save the roof I do not know. We certainly should not jump to conclusions about it, because in some of the latest work in America on oxygen it has been found that there is not so much need to be anxious about the roof as was thought.

Mr. R. WALKER (The British Coal Utilisation Research Association, London): I should like to reply to the question on the fluctuations in heat-flow-meter readings. Reference has been made to some tests made at the Appleby-Frodingham works, where producer-gas operation was compared with mixed blast-furnace and coke-oven gas operation. We found that there was no significant difference in the fluctuations when using either of these gases. The fluctuations encountered are, I believe, amply accounted for in this Report; they were due to the multiple effect of preheat, variations in the calorific value of the gas, and so on. Charging was the only factor which gave a consistent variation in the fluctuations; a considerable drop in the readings was recorded as the charging pan entered and remained in the furnace. The readings rose again to approximately their previous level as the pan was withdrawn.

Dr. CHESTERS: Mr. Halliday did most of the preheat work, and perhaps he would reply on that.

Mr. I. M. D. HALLIDAY (The United Steel Companies, Ltd.): There are three points in Dr. Leckie's remarks on which I should like to comment. First of all, I certainly do agree, and I think that it is emphasized fairly strongly in the Report, that air infiltration occurs mainly through the doors. Unfortunately, there is no accurate method at present available by which the air coming through the checker walls and other parts of the flue system can be measured, and in the absence of suitable methods of measuring such air, as against the proportion coming in through the doors, we did not go into that question; but we certainly do think that the greater part of the air inleakage is cold air entering through the doors, cooling the furnace, cooling the flame, and cutting down to some extent the speed at which the furnace works.

Secondly, the suction pyrometer has been described elsewhere as the Schack pyrometer, but it is not really a Schack pyrometer; it is a pyrometer which has resulted from the work of several people. In particular, with regard to the type of hood we used, we felt (and I think this is proved in prac-

tice) that the simpler the design, the better. Most materials when they are at temperatures above 600° C. are, in a physical sense, opaque to radiation, and our simple thin tube was quite an efficient radiation shield. The solid-angle through which the sheath covering the thermocouple views the wall in front of it, looking through the open end of the tube, is of the order of 15° to 18°. The sheath was 1½ in. back from a ½-in. aperture, approximately.

The accuracy with which this shield acted during recording may be a little doubtful. We were not able to make very special calibration tests, because of lack of time. We agree that the use of a nest of tubes would be very desirable, but almost impossible to maintain as a recording instrument throughout a charge.

Thirdly, Dr. Leckie, with regard to Fig. 43, points out that the difference between the optical and the suction-pyrometer readings was, in the case where the gas temperature is higher than the surrounding walls, only very small, about 10° C., but of the order of 250° C. where the gas temperature is low compared with the surrounding walls. I think the answer is that the radiation of the outgoing waste gases causes a surface heat which is higher than the real temperature of the walls, and as a result the apparent temperature of the wall surfaces is something nearer the gas temperature. In the opposite case, when the incoming air is colder than the walls, there is not such a great surface chill compared with the inside of the wall; the air takes relatively less heat from the walls owing to its smaller absorptivity, and the temperature difference is apparently large.

Finally, I should like to add a comment to the remark of Dr. Chesters with regard to preheat, that about *half* its value is due to the preheating effects of the uptakes. Compared with the checkers, I submit that these effects cause a large part of the preheat, but just what proportion is not known. The figures bear out that it may possibly be of the order of one-third, rather than a half, but it is not easy to assess this fraction. On the basis of temperature as measured with suction pyrometers, I do not think that the effect of the uptakes and end walls can be more than compared with the general effect of the checkers; in other words, I do not think that we can do without checkers altogether.

Mr. F. FEREDAY (The British Coal Utilisation Research Association, London): Dr. Leckie raised the question of whether changes in the air/gas ratio and/or changes in furnace pressure might account for some of the residual variation in downward heat flow. This is quite possible, but owing to pressure of time no attempt was made to investigate this possibility. In any case, the residual variation left after the effect of preheat

and sensible heat was removed was so small that errors of observation could very well account for nearly all of it. These errors might thus mask any further contribution to the variation from changes in furnace conditions.

Mr. Robertson raised the question of the number of charges considered and said that he wished there had been thousands instead of the actual 14. All the statistical results given in the paper are accompanied by a significance figure which takes full account of the number of observations and it is unlikely that much more information would have been obtained by using more charges. More computational work would be involved with a consequent increase in the time taken for the analysis; in fact, in the present analysis, only a few of the 14 charges were used in many cases.

Mr. Armstrong questioned the regression method. To deal with that problem fully would take most of the afternoon but, briefly, I think that the regression method does give a broad picture of what is happening and enables an estimate of one variable from another known variable to be made within known limits of accuracy. It is, however, important to observe that the existence of a significant regression line does *not* imply, *a priori*, a linear relationship between the variables.

In section (c) of Appendix I. to Section II., Part 11, of the Report, there was some doubt expressed as to whether the correlations observed between the downward heat flow at the centre and that at the outgoing end of the furnace was a true flame effect or whether it was due to a steady influence of roof radiation. Since this section of the paper was written, each of the 14 charges has been analysed from this point of view and it appears, by pooling all trials, that there is no significant correlation between the roof and the downward heat flow at either the middle or outgoing end of the furnace. It follows, therefore, that, on the basis of these 14 trials, the observed correlations were not influenced by roof effects.

THERMAL CONDITIONS WITHIN THE OPEN-HEARTH FURNACE.

Mr. M. W. THRING (The British Iron and Steel Research Association, London): I do not apologize for giving a theoretical talk, because I feel convinced that theory is absolutely essential for work of this kind, and in fact much of the criticism, such as that of Mr. Robertson, that we did not do enough trial casts, is answered by the fact that the work is backed up by theory. It is backed up by the theory to which it has given rise, and that enables us to make the conclusions very much more definite.

I should like to say a little about the measurement of the flame radiation, because several

speakers referred to it in the earlier discussion. Dr. Chesters has given a very clear description of the heat-flow meter and the front-wall radiometer, but Dr. Leckie suggested that it might be useful to put the roof calorimeter (which is really a heat-flow meter located on the end of a tube instead of at the side of a tube) in the ramp or roof over where the flame goes into the furnace, and so measure the flame radiation continuously and record it. Any instrument which is to read flame radiation, however, should see the flame with brick wall behind it, because the brick-wall temperature is governed by the general radiation conditions in the furnace—that is, by the flame radiation and slag radiation—and therefore is a measure of what we are interested in. If you look at flame with brick behind it, therefore, you get a fair reading, but if you look at flame with slag behind it you will not; you will be reading the condition of the bath as much as that of the flame in which you are really interested. Any instrument, therefore, to measure this downward heat flow, or anything corresponding to it, should be sighted through flame at brickwork.

Moreover, it must be fairly well along the flame and not right at the beginning, because if it is right at the beginning the flame will not have developed, and you will not get a proper reading.

It was mentioned in the earlier discussion that the narrow-angle radiometer had not fully answered the question of separating flame temperature and flame emissivity; that is, of deciding, when you have a high downward heat flow, whether it is due to high temperature or to high emissivity. The narrow-angle radiometer did, however, show the flame to be practically non-luminous at the outgoing end but highly luminous at the other end, and that has cleared the way for a further attack, which is now being made. There are various lines of improvement which will be tried; one is to use an extension of the water-cooled-tube idea to its logical extreme. A calorimeter enclosed inside such a tube is inserted into the furnace, and through it a sample of gas is sucked so that it is not the temperature of the gas but its sensible heat which is measured. That instrument, being water-cooled, can work with gases at any temperature, and will give exactly the information that is needed for constructing an accurate heat balance. It has the further advantage that if you put it in the outgoing port it tells you the heat carried out of the furnace by waste gases per unit volume, which is the figure that you want for an accurate heat balance.

The other instrument is a suction pyrometer which instead of using a thermocouple uses a permeable target through or past which gases are sucked and on to which a very narrow-angle radiation unit at the other end of the usual water-

cooled arm can be sighted. Instead of having to use a thermocouple the radiation is measured from a black-body, shaped refractory target on the end. That instrument will be limited only by this refractory unit, which can be cheaply replaced, and it will give a direct reading of the temperature of the gases. Those two instruments may in future work enable us to sort out temperature and emissivity more fully than was possible in this case.

I do not agree with Mr. Armstrong on the question of keeping the gas in the furnace for a given time. It is a question of mixing the gas and air as soon as possible so that they are burnt, and then all that they have to do is to give up their heat by radiation as fast as possible.

Mr. T. LAND (Research Department, Messrs. William Jessop & Sons, Ltd, Sheffield): My admiration has been very much excited by this series of investigations not only because of the excellent experimental work which has been undertaken, but also because at the same time the theory has been carried forward. I should like to congratulate Mr. Thring especially on the very useful and notable advance which he has made in the theory of the open-hearth furnace.

We have, during the last five or ten years, developed satisfactorily the technique of measuring the temperature of the liquid steel in the melting furnace. We are now advancing to the further stage of controlling the rate of change of that temperature, that is to say, the rate of heat input into the steel. We are faced with the question of what are the logical measurements to make in order to determine and to control within reasonable limits the heat input into the steel. In considering this question I am expressing a personal and possibly a premature view, but I feel that in the discussion of a paper one may be allowed rather more latitude than the author would permit himself.

On looking at Fig. 132 we find the downward heat flow plotted against the roof temperature, and for a given slag temperature we find that there is practically a straight-line relationship between the two. It is really a straight-band relationship, but the band is fairly narrow, in view of the limited variations of emissivity which are likely to occur.

It will be seen that the actual net heat transferred to the steel is proportional to the difference in temperature between the roof and the slag. Two different slag temperatures are considered, one of 1400° C. and one of 1600° C., and in each case we have the same relationship. It is to this relationship that I would direct particular attention. Mr. Thring has not gone so far as to derive the relationship explicitly in his theory, although it is implicit in equations (1), (2), and (3) on p. 176, and we may write down from those three equations,

merely eliminating the radiation from the flame, R_f , the equation :

$$NS = (2 - e)(R_r - R_s) + NR.$$

Since the temperature of the roof and the temperature of the slag are reasonably similar, we can go further and write :

$$NS = 4\sigma T^3(2 - e)(T_r - T_s) + NR.$$

As Mr. Thring has shown, the net heat given up to the roof is very small, and we will ignore that at the moment, so that the relationship is that the net heat transferred to the steel is proportional to the difference in temperature between the roof and the slag.

This relationship is derived for the simple case that Mr. Thring has considered of infinite parallel surfaces separated by a uniform flame. I think that it would be very helpful indeed to develop

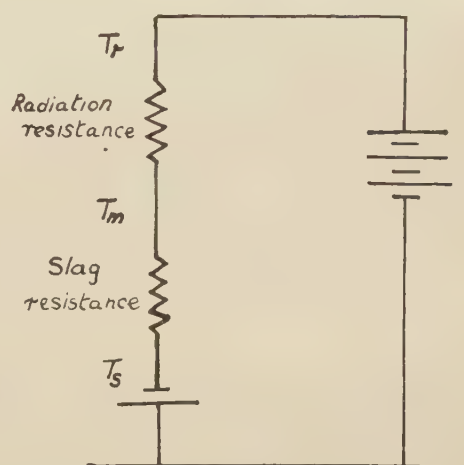


FIG. E.

the theory of radiation interchange within an open-hearth furnace to a stage a little nearer to the actual case that we have in mind. I do not propose to attempt such a development this afternoon, but I believe that it is possible to get much nearer to it without making too many assumptions. I have made a few preliminary calculations, and it does appear that the same type of relationship holds, and speaking generally the net heat transfer to the steel can be stated in terms of the difference in temperature between the roof and the slag.

This leads to a simple electrical analogy which may be helpful in dealing with this problem, since it helps to give us a picture in our minds of what is happening (see Fig. E). Suppose we start with a condenser. The capacity of the condenser represents the heat capacity of the bath. We also have a source of e.m.f., which represents the force which drives the heat into the steel. In our analogy the e.m.f. or potential represents the temperature and the electric current represents the rate of heat flow. We can now draw two resistances, and then in our simple case we can say that the potential

T_r represents the temperature of the roof, T_m the temperature of the metal, and T_s the temperature of the slag. We have two thermal resistances, a relatively fixed one, which represents the radiation resistance, and a variable one which represents the slag resistance.

From the detailed figures given by the authors it is easy to see that in the earlier stages after the metal has melted, the slag resistance is small. The reason is that the chemical agitation due to bubbles of gas coming up through the slag keeps the slag constantly circulating, and the heat transfer proceeds by forced convection; but as the chemical reactions in the metal die down the slag becomes nearer and nearer to a quiescent liquid, and the slag resistance becomes the controlling factor. In my opinion in the final stages the slag resistance greatly predominates over the radiation resistance in the furnace.

That is a tentative picture, and may need a good deal of modification before we can take it as being true, or even as being a satisfactory picture; but I thought it worth while to put it forward for consideration as a line of thought. It does lead to the view that roof-temperature measurement is not merely a matter of saving the roof from damage, but that a measurement of the roof temperature in conjunction with the measurement of the temperature of the metal may be the logical approach to controlling the heat transfer to the bath.

Here I think that my ideas are likely to come into conflict with those of the authors, who give me the impression that they look to the front-wall pyrometer or radiometer for a measure of the heat transfer to the bath. It is a very tempting idea, but my impression is that Mr. Thring in his theory has given a considerable amount of evidence that the roof is the correct point for measuring the heat transfer to the bath.

Dr. A. H. LECKIE (The British Iron and Steel Research Association): Mr. Thring has developed a very convincing and simple theory of heat transfer in open-hearth furnaces, and he has shown that proper heat release depends on two factors. One is that the gas and air must mix completely, and the second is that the heat must be released from the flame to the charge. Those are common-sense fundamental assumptions. With regard to mixing, I think that the authors as a whole have rather over-emphasized the correlation between the heat flow at the middle door and the end, as compared with heat flow at the middle door and entering door, because one would naturally expect that only a proportion of mixing would have taken place by the first door. I am wondering whether even with the best port one could get one would expect a reasonable amount of mixing by the first door.

I am also wondering whether Mr. Thring is right in dismissing so rapidly the concept mentioned by Mr. Armstrong of the importance of the time that the hot gases stay in the furnace. It is significant in the minds of a great many practical melters, and, while it is difficult to give a good reason why it should be important, we have not yet heard a good reason why it should not.

Taking the results on the experimental furnaces, we find that *K* furnace, the Maerz, gives very good overall mixing, but, owing to the fact that the mixing is at the top of the flame as well as down below, there is a danger of damaging the roof. On *S* furnace, mixing is confined to the bottom of the flame, and the layer of cold air on top protects the roof. On the strength of that, the authors regard that furnace as the best of the three; but it is a great pity that its advantages should depend on the presence of a layer of relatively cold air—*i.e.*, air at about 1200° C.—on top of the flame, which must go through without doing any work, apart from cooling. If it is indeed necessary to cool the roof in this way, is it not possible to do so by admitting a controlled small quantity of air under the roof, so that such a large excess is not used merely to keep the roof cool?

On p. 143 it is suggested that the good mixing on *S* furnace is due to the vertical cheeks throwing the air inwards towards the gas, and on *K* furnace to the use of air streams directed vertically upwards at right-angles to the gas. I would agree to what is said about *S* furnace, but I do not think that I can accept the argument for *K*, because in the drawings the uptakes are very small, and the air jets emerging from the top of the uptakes will not come into contact with the gas which is issuing from the port for some time. It is more likely that the good mixing in *K* furnace is obtained because the gas, immediately it leaves the port, emerges into a very large space, free from all restrictions. In the paper by Davis (*loc. cit.*) the diagrams show how necessary it is for a jet emerging from a port or orifice to have as unlimited access as possible to the surrounding atmosphere if it is to mix with this atmosphere. That is obtained in the *K* furnace, and I think that is the explanation of the good mixing.

Mr. Thring has made a suggestion for a very good design of port, and his reason for that is that you get a high velocity on the ingoing gas without introducing too much resistance to its handling of waste gases. That is going on the principle, as Rummel shows, of the necessity of high velocity in the gas port; but there is another principle which comes in, that the mixing length of the flame depends on the diameter of the gas port, and that brings us back to the suggestion that it might be an advantage to go back to a type of port used in a great many early furnaces, *i.e.*, dividing the

gas between two or even more ports. That type of construction was, I believe, abandoned early in the history of furnaces because of difficulties of maintenance; but with modern refractories and judicious water-cooling it might be possible and desirable to go back to the use of more than one gas port.

With regard to heat release, I am wondering whether Mr. Thring's concentration on radiation is not an over-simplification. Certainly, if you calculate convection and radiation on the basis of ordinary heat-transfer laws, convection is a very small proportion of the total heat transfer at the temperatures of furnace operation, but in practice you get a blowpipe type of flame impinging on a pile of scrap it will cut that scrap down very rapidly. That cannot entirely be convection, and I am wondering whether there is a completely new factor coming in, such as surface combustion, helped catalytically by the scrap itself, by oxide on the scrap, and so on.

Considering Table LXXIX., tests *H4* to *H6*, it will be seen that the average net downward heat flow is 80 units. If that is worked out for a bath of 330 sq. ft. it comes to an average of 107 therms/hr. The melting load for *H* furnace is in the region of 1,000 therms, so that you have to melt 1,000 therms and there are 107 therms/hr. with which to do it, which means a melting time of $9\frac{1}{2}$ hr. The actual time was $7\frac{1}{2}$ hr., and, allowing $1\frac{1}{2}$ hr. for the effect of charging time, that comes down to a period of 6 hr., so that the melting has taken place at a very much quicker rate than the measured downward heat flow would indicate. That may be due to some other factor, such as the surface combustion, as I have suggested, or to the fact that the heat-flow meter cannot be put in at the charging period, when the scrap is piled up, yet that is the moment when the heat transfer to the stock is most rapid, owing to the large temperature difference between flame and stock.

Mr. Thring does not explain clearly the relation between roof temperature and downward heat flow. He suggests that the roof cooling brought about by increased area, associated with a sloping back wall or a higher roof permits of several more units of downward heat flow in the furnace, but later he suggests that heat flow through the roof is not important. Surely it is important, however, if by getting slightly greater heat loss through it you permit greater downward flow? I agree with Mr. Land that roof temperature in itself must come into the picture somehow.

There is one interesting fact that I should like to mention, though I am perhaps anticipating future publications. The experimental furnace at Shelton is a one-way furnace; we measure the temperature in the roof in a number of places, and the quantity of heat transferred to the hearth in four sections. Being a one-way furnace, the roof

temperature is always very much lower at the incoming end than at the outgoing end, owing to the slow development of a diffusion flame. Yet we find that the amount of heat transferred to the hearth at the ingoing end is less, but not substantially less, than the heat transfer at the outgoing end. That suggests that radiation from the hot roof at the outgoing end on to the cooler hearth at the ingoing end does come into it, and I think that it would be rash to say that the roof temperature does not come into the picture.

All the recent researches on open-hearth furnaces have shown that one of the most important things is the correct control of combustion, rather than getting the maximum gas into the furnace. With correct control the same amount of heat can probably be got into the charge as with a much larger quantity of gas and with less control.

Dr. H. R. FEHLING (London): A tribute is due to this undertaking as a whole; it is a splendid example of good team-work. I think that we are witnesses here of the opening stages of a great campaign, which originates from a series of challenges which this team has been prepared to meet. As Dr. Chesters so rightly said, it is Fig. 1 of this Report which constitutes the main challenge. The second is the low thermal efficiency and the appalling heat losses, and the third is, of course, the limited life of the structure as a whole.

There are many reasons why there has been so little spectacular advance, but three at least are, to my mind, outstanding. The first is obvious to any one who has operated high-temperature furnaces, in which the main structure is exposed to the corrosive and erosive action of slag. This is very familiar to you all, and does not require further comment, but the two others are less obvious.

In the first place, there has been a lack of experiments on a really large scale, such as the one under discussion. The argument has always been that they are too expensive. Dr. Chesters and Mr. Thring should one day work out the cost of their experiments and set against it a conservative estimate of the economic gains which would accrue to the steel industry if they adopt their most elementary recommendations, those, in fact, which could be introduced in any steelplant tomorrow with the minimum amount of instrumentation. I believe such a calculation would prove that such large-scale experiments, provided that they are carried out and properly evaluated by intelligent people with a maximum of speed, are, in fact, a very good paying proposition.

The third of the reasons to which I referred is that for many years there has not been a sufficient insight into the major importance of the physical aspects in the field of combustion and furnace technology, and therefore there has been a lack of

model technique. As is well known, model technique is the most important single factor in the development of many branches of technology, *e.g.*, hydraulics and aeronautical engineering. When applied to furnace technology, many still regard this technique as purely academic. In fact, it is nothing of the kind; it is a tool for breaking up the complex problems in the actual furnace into a number of controlled experiments yielding certain information which can be translated back into full scale, and usually produces results for one-tenth of the cost, within a much shorter time.

I therefore agree very strongly with Mr. Thring when he says that the next step is not to make a thousand casts instead of fourteen, but the intelligent application of model technique. These model experiments will have to cover the whole range of aerodynamic, thermodynamic, and mechanical problems, which the authors have defined as a result of their investigation.

In my view this Report crystallizes the paramount importance of two critical temperatures on which nearly everything else depends: The maximum combustion temperature and the maximum permissible roof temperature. As the authors state, the increase of the theoretical combustion temperature is the most important single factor in raising both output and thermal efficiency. This is very important, and less obvious than it may sound. No one has yet stated so clearly that it is the decisive factor for raising both output and efficiency, and not only one of the two. I was surprised that the authors mention only two of the three possible approaches to increase the combustion temperature. Apart from preheat and air/gas ratio, there is the possibility of increasing the calorific value of the gas.

As long as we contemplate producer gas as the basic and cheapest fuel for steelmaking, it would be unwise to separate the efficiency of the furnace from the efficiency of the producer. If we want to save fuel we must save not producer gas but producer coal, which is not the same thing. If the calorific value of the producer gas were raised by preheating the blast, not only would this improve the efficiency of the producer, but it would also raise the furnace efficiency at the same time, owing to an increase of the theoretical combustion temperature.

Some years ago Dr. Rosin and I prepared a report for the Iron and Steel Federation, in which we worked out that by preheating the blast and increasing the steam/air ratio one might hope to increase the calorific value of producer gas by as much as 40 B.Th.U. The combined increase in efficiency of both the producer and the furnace should result in a saving of producer coal of up to 25%, due to the thermal factors alone. We are now told by the authors that by increasing the theoretical combustion temperature we shorten

at the same time the melting time, which apart from increasing the output, will certainly decrease the wall losses, not per hour but per ton of steel, so that the overall increase in efficiency should be much more than that due to purely thermal efficiency.

The critical character of the permissible roof temperature has been brought home by this Report. It is clear that the development of new materials which could stand 50° C. more than those now available is a subject of such importance that I do not think that the cost of research comes into it at all; I think that someone should be given *carte blanche* to solve the problem. There is, however, one aspect which has not been emphasized in the Report. Mr. Thring quite rightly said that the thermal conductivity of the roof is such that the heat flow through it may be a negligible part of the gross radiation, but this does not mean, of course, that the heat losses through the roof are negligible in the total heat balance, and a big problem is the development of an insulation material in order to minimize this loss. If a super-refractory insulating brick could be developed I am sure that we would have the principal element of a new furnace.

I want to mention one other point, and it is one which was brought up by Dr. Leckie when he said that in his opinion Mr. Thring had underestimated the influence of convection. There is a great difference between the convection of hot gas and the convection of a flame.

Let me give an analogy. In heat transmission one knows the enormous difference between the rate of heat transmission of a condensing vapour and of a gas, and the reason is that the latent heat of condensation is, as it were, "deposited" on the surface with a very high rate of heat transfer which has nothing to do with the conductivity of the medium. Similarly, if a flame impinges on a surface the heat of combustion is, as it were, "deposited" on this surface. Again, this type of transfer has nothing to do with what is normally called convection or radiation in pure heat transmission.

It is difficult to resist the temptation to discuss a Report of such exceptional scope and merit in much greater detail. But there will, no doubt, be many other opportunities in the years ahead when, step by step, the development on a grand scale of one of our main industrial processes unfolds. I hope that at the end of the campaign, which will tax the ingenuity and fire the imagination of many physicists, chemists, and engineers, we may see a new furnace, something which represents a fundamental improvement on the original Siemens design.

Dr. D. H. BANGHAM (The British Coal Utilisation Research Association, London): I have nothing

of scientific interest to contribute, but I would like to describe briefly the history of this work from the B.C.U.R.A. standpoint. I think it was Dr. Sarjant who first drew Mr. Thring's attention to the advantages to be gained from determinations of the heat flow in open-hearth furnaces. Work was begun in quite an amateurish sort of way, but, with a little ingenuity on the part of Mr. Thring's team and with help from a panel which met from time to time under Mr. Wardley's chairmanship, it was not long before an instrument had been constructed that would survive the very severe conditions imposed. It was at this stage that the Association was approached by The United Steel Companies, Ltd. (in the person of Dr. Chesters), and invited to collaborate in planning and carrying out this very imposing series of large-scale experiments.

I think it must require a good deal of faith to embark upon such a large and elaborate programme for the primary object of obtaining basic information, but it is clearly in that direction that progress lies. Perhaps, in the past, industrialists have lent too ready an ear to inventors holding out promises of increased dividends in one step, the inventions, however ingenious, being mostly shots in the dark; the scientist, pleading for enterprise or expenditure aimed at obtaining fundamental data *upon which inventions could be based*, often got rather a poor hearing. After all, knowledge and experience are worth paying for, and provided that industrial experiments are well planned, the results are bound in due time to bring their reward; the element of risk is eliminated.

MR. THRING (in reply): I shall not attempt to answer all the points which have been raised, but one or two of them are of special interest. I am very glad indeed that Mr. Land is extending this theoretical treatment and applying it more fully than I tried to do, and I hope that I shall be able to have many fruitful discussions with him on that matter. The most important point which I should like to answer is on the question of measuring the heat transfer to the bath and the method by which it should be done. He said that the roof pyrometer is the way to measure it, and I said that the measurement of the flame with the roof or back wall behind it is the method. He is quite right, and I am quite right.

It is like this: If you have a given steel temperature, then there is a relation between the roof radiation (and temperature) and the flame-plus-roof radiation which is fixed within certain fairly narrow limits.

If you lower the steel temperature you can have a higher flame radiation for a given roof temperature, and there are slight variations which you can make by running with a different kind of flame. Thus, if you have a given steel tempera-

ture and a given roof temperature and you want to get the greatest possible heat into the bath, you should do it with a more transparent, hotter flame and not a more opaque, colder flame. That is strictly within the conditions that I have mentioned, because with the more transparent flame the roof is more effectively cooled by the bath, and therefore you can have more excess flame radiation than in the other case. When the roof is on limiting temperature it may well be better to reduce the emissivity of the flame rather than the temperature.

It is for that reason that I say that on an ideal furnace you would measure the roof temperature *and* the flame radiation, but certainly the roof temperature has to be measured first; the flame radiation measurement is a luxury, but a luxury which is of value, because ideally one would say to a furnaceman, "Get your roof temperature up and keep it on the line. When you get it up to the line, try to rearrange your conditions to get the flame radiation as much above that as you possibly can, and then you will get the greatest possible heat into the bath."

A very interesting point is that this front-wall pyrometer on every reversal came down to the roof temperature, showing that the back-wall temperature is exactly the same as the roof temperature, and that it is simply the flame in between which gives this rise, but nevertheless it is the roof temperature which limits the flame radiation temperature. Can you, by manipulating the controls, get the total radiation up to a higher figure? Until the instrument has been installed on a number of furnaces it will not be possible to answer that question.

I put forward the plea, therefore, that instruments on furnaces should be regarded as being in different categories. There is the category of instruments which we should like to see on every furnace: Measurement of the roof pressure, in order to control the air going in, gas and air measurement, waste-gas temperature, and so on. That is the first category.

Into the second category come one or two luxury recorders with which one furnace in every melting shop should ideally be equipped, to see their value in practice. They are the CO₂ meter and the front-wall pyrometer reading the radiation of the flame. The third category consists of the research tools, the instruments of the "Harley-Street specialists," such as the water-cooled probes, the heat-flow meter, the narrow-angle radiometer, and the suction pyrometer. I put forward the plea for three categories of instruments: Those for every furnace, those for one furnace, and the special research tools that come out when there is some special problem to which an answer is wanted.

I entirely agree with Dr. Leckie on the question of different shapes of port and the possible use of

two or three gas ports. It is a purely practical problem; on the theoretical advantage I agree. Another way is to use a flattened gas port, extending nearly from front to back of the furnace and very shallow in vertical height so that the area is normal. This would reduce the distance across which the air has to mix with the gas and give a greater flame radiation across the bath at the incoming end, where it is most valuable, but might give trouble with burning the front and back walls. But the answer which all this discussion has brought out is that we can think of a number of possible improvements in port design, and they must be tested on models and the advantages assessed before the actual building takes place.

I agree with Dr. Leckie and with Dr. Fehling in saying that where you have impingement of the gas on a surface of piled-up material, convection and special mechanisms—surface combustion or unloading of stored-up energy in the gas—can come in and give abnormally high heat transfers, and you can have actual oxidation of the material, which gives very good heat, the heat released by this reaction being directly available for heating it up. The calculations described in the Report were concerned mainly with the case when the bath was fairly flat, because that first period of cutting down the scrap is not such a problem, since the surface to which heat is being transferred is fairly cold at that stage.

I still stick to my disagreement with the two-seconds idea. I think that the whole problem should be looked upon in terms of mixing and combustion and heat transfer, and that any empirical rule such as that is merely a way of ensuring that those conditions are satisfied which have worked in practice in the past but do not necessarily need to be adhered to when better ways of fulfilling those conditions are available.

Dealing with Dr. Fehling's point about calorific value, I would draw attention to Table LXXXV. The question of lowering the calorific value, not raising it, was calculated there. As between case 1 and case 7 everything is the same except that the calorific value of the gas is 20 B.Th.U. lower, and the drop in the theoretical combustion temperature by lowering the calorific value 20 B.Th.U. is from 2320° C. to 2230° C., which, while quite significant, is not as great as the difference between case 1 and case 3, which is due to the introduction of an extra volume of air equal to half the volume of gas which is not preheated in the checkers and leaks in through the doors. Therefore, it is necessary to put our house in order as regards air infiltration before the calorific value is regarded as the primary method of improving performance. Roof-pressure control is solely to reduce air infiltration into the furnace, but for that reason it is essential.

GENERAL CONCLUSIONS.

Mr. W. GEARY (Appleby-Frodingham Steel Co., Ltd.), acting as rapporteur, said: A melting-shop manager, on receiving a report of this magnitude, will most probably ask himself what it contains that he can apply to his plant; he will look first for anything that can be done at once and then for suggestions of things that need more time. With this in mind, I propose therefore to refer to one or two of the findings and recommendations of the Report. Output naturally is one of a melting-shop manager's chief preoccupations, and, in an attempt to show what the trials indicate in this respect, I have assembled a few figures.

The past performance of the trial furnaces was examined by statistical methods, and the results are reported in Section I., Part 2. The examination covered a period of eighteen months before the trials, and the results included not only figures of average working rates, &c., for full campaigns, but also rates achieved when the furnaces had new checkers and roofs. It was assumed that they were new for 8 weeks after installation. This latter figure is therefore one with which the trial results may be compared; the result of such comparison is shown in Table A. It will be seen that

TABLE A.—*Output Rate of Trial Furnaces Compared with Previous New-Crown-and-Checker Periods.*

Furnace.	Previous Periods, tons/hr.*	Trials, tons/hr.	Increased Rate, %.
H	7.3	8.1	11
K	7.5	8.7	16
S	8.9	10.1	13

* Rate of working is from start of charging to tapping.

there is a considerable gain in average working rate under the trial conditions. We do not doubt that such a gain would be welcomed by any melting-shop manager; we go further and say we believe that anyone can make a gain if he will bring the amount of control on his furnaces up to the standard we used during the trials. I would remind you that this morning Mr. Robertson has said that if our basic principles of control were properly used by a shop manager, the output of most British furnaces would be increased by up to 50%.

Now, it might be suggested that whenever one sets out to get a "flying charge" it can always be done. It may be suggested that our use of special scrap as against the ordinary run of merchant scrap was unfair and would tend to influence the performance in the direction of fast working. We realize that there was, in fact, a gain in speed from the use of this special scrap. Our object in arranging the supply was to standardize as far as possible the composition of each charge in the trial series.

Arrangements were also made that the steel specification should not vary much from cast to cast; and thus by controlling the composition of input and output, the variation of the metallurgical factors was kept within such reasonable bounds that their influence could not mask the main results. The amount of time that was saved by the special scrap was approximately $\frac{3}{4}$ hr. on the charging-plus-melting time. The evidence for this statement is given in Section II., Part 8 (calculation of slag burden), and from Fig. 128. The scrap was from the Companies' section mills; as has been said, its composition was substantially constant, but it was not unusually suitable for packing into charging boxes, in the way that bloom crops may be used to get a very fast charging rate.

The statistical examination previously referred to has shown that, in any case, the charging rate itself has not a predominating influence on the overall rate of working. Mr. Armstrong has already told us that he had himself reached the same conclusion. It is shown that in the *non-trial* casts, charging time was 13% longer, melting time 38% longer, and refining time 15% longer.

The conclusion that the authors draw from all the above evidence is that, out of the total saving in time of $1\frac{3}{4}$ hr., $\frac{3}{4}$ hr. is owing to the influence of the special scrap; while the remaining saving of 1 hr., principally in melting time, is the result of the instrumentation, or rather, the control which was made possible by instrumentation. In other words, the control that was put on the furnaces turned them into better steelmaking tools. Dr. Chesters and Mr. Thring have made it clear why the furnaces became better steelmaking tools—because they were able to transfer heat to the charge more quickly than they had been able to do before.

I am convinced that one of the most important things in getting the maximum out of a furnace is to keep the CO_2 high in the waste gases, but this high CO_2 is probably the hardest thing there is to get and to keep.

I do not suppose that there is anyone who has run furnaces who has not at some time or other contrived an improvement by conducting a campaign on his waste-gas CO_2 . Since the control of furnace pressure is of paramount importance in this, we suggest that the successful application of fully automatic roof-pressure control would bring notable savings to the steel industry, since by that the most important factor in the attainment of high heat economy would have been established.

I think all steelmakers are now agreed that gas and air should be measured; the evidence of these trials must have helped to remove doubt from the minds of those who did not think hot producer gas could be successfully measured. The advantage of knowing also the calorific value of the gas will, I think, be admitted, and we regard our results with this measurement as most encouraging.

Measurement of gas quantity and quality would seem to be complementary to the measurement of roof temperature.

It has been suggested this morning that in the trials we did not work with our roof temperatures high enough. It is just possible that we could have worked safely at slightly higher temperatures, but we chose our maximum with the idea of running the furnaces as hot as possible with safety, thus taking no risk of reducing the value of our results by burning furnace roofs. At the same time, it is reasonable to suppose that, with more experience of full control, it will be possible to set higher temperature limits, and in view of the very large increase in downward heat flow that comes from a comparatively small increase in roof temperature, it seems likely that much faster rates of working will be attainable.

I must call your attention to the work done by Mr. Halliday on preheat. The figures he obtained are, I think, new to most people. I do not think that we realized what the real values were, nor do I think that it was previously known what large variation there was in heat transmission to the bath at the ingoing end, as the preheat varied. In between each reversal the preheat fell away, and there was a substantial drop in downward heat flow. The Report suggests that it might be worth while considering again automatic reversal by waste-gas temperature difference. I think the figures suggest that more frequent reversal would be advantageous, but that question brings in its train others, such as getting valves which will work more quickly, so as to cut down the loss of gas to the chimney.

In The United Steel Companies we are continuing the work with the front-wall pyrometer. Since this instrument records flame conditions as well as the general conditions inside the furnace, we do not see why it should not eventually become a master instrument that will give the melter an early indication of a change occurring inside his furnace. It would probably not tell him what the change was, but would lead him at once to consult his other instruments, which would probably show him the source of the alteration.

The Report recommends strongly that all instruments and controls should be brought into one central place from which the melter can supervise the operations. It should be made unnecessary for melters to open their furnace doors as much as they habitually do in most British practice. A frequent comment made by American and pre-war Continental operators is that we open our doors far too much. Mr. Halliday's work brings out an interesting point in this connection, where it is shown that the influence of the door being opened does not cease as soon as it is put down again, but persists for as much as an hour afterwards.

The best of our trial furnaces was the one in which the necessary amount of gas could be burnt in a comparatively short flame, and this was the one that gave the most pronounced vertical stratification. We know that the vertical stratification helps to give a high flame temperature and at the same time preserve the roof from the full effects of it. In this connection Dr. Leckie's comment this morning was particularly interesting. He suggested that it seems unreasonable, if we must have a layer of air immediately under the roof, to put it all through the furnace system, and he suggested that the object could be attained quite as well by spraying the air layer underneath the roof from suitable jets. This possibility had already occurred to us, and we shall certainly keep it in mind.

However, we suggest that the high performance attained by *S* furnace can be largely accounted for by the factors which produced the vertical stratification. It may also be that *S* furnace, with the type of flame it can develop, will be rather more adaptable either to straight scrap melting or to refining. It is believed that this type of flame is capable of rather more modification than that of the other two furnaces.

You will notice from the reports of *H* furnace that the flame tended to be long, except in one or two charges. It was rather a soft flame, the type which gives a lower radiation to the bath than the others. The *K* flame, which was definitely non-stratified, and was at a high temperature, was inclined to be a little sore on the roof.

The authors and their collaborators are acutely conscious that they know only too little, even after all their work, of what makes a good port, and they realize very clearly that much more work is needed. Several of the speakers have made mention of models, and the authors are in hearty agreement with this suggested approach. In fact, work on models is already in hand and further work of the kind is projected.

Dr. R. J. SARJANT (Messrs. Hadfields, Ltd., Sheffield): The sponsors, authors, and the large team of observers who have worked on the difficult technique described in this Report are to be congratulated on producing so much interesting information. A busy man might wish that the Report could have been boiled down to something more readily assimilated, but it is of value that the information has been collected, recorded, and made available for those who are interested in the subject.

The Report emphasizes in a most important way the value of plant-survey work. Many of us have hammered away at this kind of problem, and know that it must have required a good deal of courage on the part of the sponsors of this work, as well as a great deal of hard work from the team

of authors and observers, to achieve the results shown. All survey work of this type is onerous. It means getting grubby all through the day and night, placating managers and others, and the results may sometimes be valueless because some instrument or other breaks down. It needs almost the heart of a lion to carry it through, and it is therefore very refreshing to find that this work has been designed on the right lines and successfully carried out.

The fact that the statistical method has been used so fruitfully is also, I think, a lesson which should be noted. It is in this class of work as essential a tool as the older instruments—the flow meters, the pyrometer, and the recording gauge—and the newer ones, such as the heat-flow meter and the radiometer.

We cannot cheat Dame Nature; she hides her secrets carefully. If many of the conclusions here represent guiding principles which have been known for years, the mere fact that a detailed series of large experiments such as these has brought out quantitative confirmation is of value, and if the results have not got to the hard core of indifference on the open-hearth stages yet, it is time that they did.

The first lesson of this Report, as I see it, is the importance of the questions of preheat, excess air, proper draughting, and the use of the right instruments. Another important outcome of it is that it shows that for getting the right draughting, which is a critical factor in any type of furnace, there is a simple instrument which can be used. A great deal of fuel is wasted in this country through improper draughting of furnaces. The Report shows quite definitely that the pressure recorder can be used for that purpose. It keeps the draughting of the furnace right, it cuts down the excess air, pushes up the flame temperature and, next to the roof pyrometer, it is probably the most useful instrument that can be put on the furnace.

It is noteworthy that the furnace which gave the highest rate of melting also gave the highest fuel consumption, based on the unit of output. It is known that optimum economy from the fuel standpoint is obtained at a critical rate of driving, which must generally be obtained by trial on the plant. Whilst it is clearly stated in the Report that in the present case the proportion of air used had a considerable effect on the fuel economy, there is, of course, an unknown factor in regard to this question of whether the furnace is being over-driven or not. Further, the condition of the charge itself has a lot to do with the economy. It is well known that it is possible to alter the time of melting considerably by variations in the class of charge and the manner in which it is put in, and those who have studied the method of charging have obtained tangible results from such investigations.

I should like to ask the authors whether in their experiments they found a point where the raising of the flame temperature changed the ratio of the sensible heat in the outgoing gases to that absorbed by the charge in such a way as to make it operate unfavourably to the fuel economy. Was *S* furnace really being over-driven, for example, from the standpoint of fuel economy? We want quick-melting furnaces and fuel economy, and the over-driving of a furnace should not be disregarded.

In this particular case I should like to know the nature of the slag, the amount of slag, and the depth of the hearth. Sometimes people talk about quick-melting furnaces and overlook the fact that the hearth is shallow. The whole of this subject is a question of dimensions. We have not heard much about that in this discussion, but furnace designers are interested in such aspects. One has to get down to calculation in this matter. It was rather deprecated in the Report, and I was sorry to see it, because it must be possible intimately to compute the derivations. There may be a lot of stratification in furnace chambers and flues, which I know complicates the issue, but if you can ultimately get at the coefficients to go into the formulæ you can put the whole matter on a scientific basis. I think that this Report is a step towards the ultimate goal, although there has been little stated about coefficients other than that of the emissivity of the flame.

There is a valuable observation on p. 44 of the Report, on the relationship between gas flow and gas pressure. That is a very useful piece of work, because it shows that a great deal of use can be made of a simple instrument, the gas-pressure recorder in the gas uptake. A curve is given of the relation between gas flow and pressure in the gas uptake, which indicates that if at the same time the wear of the ports is watched, a simple means of measuring the gas input to the furnace is obtained.

Observations which have been made of the heat exchange against the distance from along the checkers show a hyperbolic type of curve, which is typical of the curve obtained in any heat exchanger. In the open-hearth furnace, radiation plays an important part in the uptakes. I believe that the old furnaces which had small slag pockets were generally—though one would be horrified to use them to-day—very hot melting furnaces. I am glad to see that the heat-flow meter has been useful. It was originally suggested as a result of the deliberations of the Industrial Furnaces Research Committee, and I am pleased to see that it has given such fruitful results.

On the question of instruments, it should not be implied that little has been done by other branches of the steel industry in these matters. On p. 161 there are four instruments recommended as essen-

tial, and I know of one works in the Sheffield district which has every one of the instruments there recommended and, further, has not only a roof-pressure indicator and recorder, but a roof-pressure controller, which controls the damper on the roof-pressure indications; and three of those instruments including this last have been installed for a number of years. Many other people have been giving these subjects a good deal of attention. We cannot all be so fortunate as to be able to put a large team of people on survey trials. Our aim can, however, be to use our instruments, not just as things for a man to look at, as he would look at a clock, but as a means of keeping and analysing records. If we have furnace records and instrument charts and examine them systematically we are really carrying out in a sense a continuous furnace trial in the operation of our furnaces.

Mr. J. T. WRIGHT (Round Oak Steel Works, Ltd., Brierley Hill, Staffs.): I have listened with rapt interest to the theorists during this discussion, and this excellent Report will be of tremendous interest and potential value to all those who are directly engaged in the manufacture of steel by the cold-pig and scrap basic open-hearth process. There may, however, be some amongst us who feel that we must not be too easily led, or misled, by the extremely efficient manner in which the technical theories have been propounded by the theorists. Some of us, like Mr. Geary, are more interested in the practical aspects of the Report, and in the outputs which we are likely to obtain if large-scale instrumentation is adopted on our own particular open-hearth furnaces.

I should like to draw attention to several practical factors which, in my opinion, may have some bearing on the very important questions already discussed. Great stress and importance has rightly been laid by Dr. Chesters and his colleagues on the maintenance of as high a roof temperature as may be considered safe, in order that the maximum downward transfer heat flow may be constantly maintained. I am sure that all of us would agree that this is obviously desirable and important, as many previous speakers have indicated. If, for example, as Mr. Robertson has said, the temperature of the roof had been raised to 1660° C. or the actual softening point of the brick, instead of 1630° C., as used in the experiments described by Dr. Chesters, this temperature differential of 30° C., between the melting point of the roof and the tapping temperature of the steel, would make a difference of from 15% to 20% in the heat-transfer rate. This temperature differential, which may exist with or without instrumentation, can therefore alone account for 15% to 20% difference in heat transfer or output, which is the same total percentage increased out-

put accredited by the authors to the furnace with complete instrumentation.

These theories with regard to flame temperature and emissivity are very important, but quite incomplete unless they also take into consideration the heat absorptivity or conductivity of the charge; and it is to this particular and important practical aspect that I should like to refer. There are many factors which can affect rapid heat transfer, other than high flame temperature, design of port, and flame emissivity. Permit me to mention a few which, in my opinion, might affect it. We have been informed that an attempt had been made to standardize the metallurgical load of the cold-charged pig and scrap furnace. I submit, despite their efforts, that it cannot be done. There is no guarantee of uniformity of the metallurgical load. In the first place, the type or character of the scrap was substantially changed by using an increased quantity or a very large proportion of mill scrap. This action, in itself, would naturally tend to equalize the metallurgical load on charges of similar proportions of mill scrap, but it would be premature, and, in my opinion, unjustifiable, to compare the speed of outputs on a similar furnace with such a dissimilar character or nature of scrap as was used. This preferential method of charging is particularly well known to many of us who have to scheme hard to get the extra cast of steel almost every Friday night, and the surest and almost certain method of doing this is by switching over from the current run of merchant scrap to clean mill scrap. This does not mean that all the scrap charged must be clean mill scrap, nor crop ends, but something of the order of about 20 tons of clean mill scrap has reduced, and does reduce, the tapping time by about two hours in every twelve, and this 16% to 20% increased output by preferential selection of scrap, irrespective of increased weight per box, is again, in itself, equal to the total saving accredited by the authors to complete instrumentation of the furnace.

The position in which the lime is charged, and the speed with which it is fluxed, is of great importance. I know full well that they would charge the lime at the same stage, as far as possible, in each charge, but the quantity of lime fluxed by the acids of the metallurgical load is not necessarily the same in apparently identical charges, and the quantity of lime remaining unfluxed determines the quantity of gas, or heat units, which any silica roof or port structure will stand, owing to the intense reflex heat reflected from this unfluxed lime. It may be, at this stage, that no further heat can be pushed at the charge as the silica roof temperature would rise rapidly to the danger softening point, and heat or gas would, and must, be slacked back. This, in my opinion, with or without instrumentation is most likely to

occur, and only the fastest possible voluntary fluxing of the lime by the addition of spar, is likely to get over this dropping of the roof temperature by the furnaceman easing his gas over the dangerous period when unfluxed lime is reflecting its highest temperature.

I submit that the drop in the roof temperature mentioned by Dr. Chesters may have been due to the more rapid absorption of heat by the bath at the period when it is opened up by the additions of spar, oxide, &c., as the absorptivity of the charge is likely to be higher when the bath is open than when covered with unfluxed lime, or a quiescent layer of semi-fused slag, &c. In other words, the flame temperature can, or would, drop, for the same B.Th.U. input, with an open slag than with a closed slag or covering of lime, and heat transfer can be even more rapidly conveyed to the charge with a lower roof temperature when the slag is open than it can with a higher roof temperature with a closed slag. The position or time of fluxing of the lime is therefore important because of its effect upon the speed of the slag formation and its consequent direct effect upon the output. A variation of one or two boxes of lime per charge, its early natural or forced fluxing effect, the time and the volume of the slag made, and a variation of slag weight of one ton in eight means a difference of $12\frac{1}{2}\%$ of the total heat units for slag formation. Such an addition or decrease of lime would indicate that there has not actually been standardization of the actual metallurgical load.

Referring to the calorific value of the producer gas and the input of heat units, I would like to ask the authors if they have taken into consideration the possibility of any accompanying water vapour. I think that the dew point of producer gas can vary appreciably from hour to hour, and has a direct effect upon the flame temperature, irrespective of similar calorific value. This variation of flame temperature from one cast to another on the same furnace, the changing emissivity, and the changing absorptivity factor of the charge, are some of the practical factors which can affect the rate of any furnace output at least equal to, or in excess of, the claims made by the authors for complete instrumentation alone.

Mr. S. W. PEARSON (Messrs. Steel, Peech and Tozer): I am glad that at least one of our friends has come in on the ground floor! Any contribution that I can make, can, of course, be only on that level. The higher storeys are left for the more intelligent and more technical people, but there are still some who have to remain on the ground, and it is as well that way.

I think that the only point that I need answer is the contribution from Mr. Wright. I can only feel that he has had insufficient time to go through the Report thoroughly. That is one of the diffi-

culties of having a rush report of this kind. If he had had more time to study the details, he would have found that most of the answers to his questions are contained in the Report itself, particularly with regard to such points as slag bulk, lime, and so on.

He was under a misapprehension about the use, or misuse, of mill scrap. Mr. Geary had said that the scrap available was not mill scrap, but a type of scrap which made it fairly easy for us to control the metallurgical burden and the method of operation. We should have liked it to be otherwise; we should have liked to have taken run-of-shop scrap; but we knew that this would introduce further variables. It was our job in the melting shop to standardize and control the steelmaking, and I can say that part of the job was comparatively easy, compared with controlling the 25 to 30 scientists, who were around the furnace, and their various instruments.

I think that most of the answers are in the Report, if you have sufficient time to find them.

Perhaps you would like me to refer to a later trial on another furnace. This combustion business puzzles many of us, and we have to think about it in our own way. Two or three ways of improving combustion are noted in the Report, and Dr. Sarjant referred to another way. To my mind, if we want to get more output we have to burn more gas correctly and propagate the flame more quickly. Better mixing will do it and better preheat will do it, but if these two factors are constant, owing to furnace design, there is yet one other item which is particularly important, and that is pressure behind the port, which of course means increased velocity from the mouth of the port. If we can achieve this, we can get an early burning and a good radiating flame with a high CO_2 figure in the waste gases, since less excess air need be used.

I believe that Dr. Leckie wrote a paper some years ago showing that, in one shop, outputs were increased as amounts of excess air were increased, but I believe that his views have been modified since that time. I think that if we can get a luminous, well-burnt flame with the maximum percentage of CO_2 in the waste gases, we shall get the best flame possible, and the best way to do that, other factors being constant, is to get as high a port pressure as possible.

With a furnace recently built in another melting shop in the same works, the only differing factor was a new gas-valve system, which cut out many of the resistances to the ingoing flow, and provided new experience as far as I was concerned. The gas port was more or less standard for what the furnace would do, and when waste-gas readings were taken we were alarmed to learn that, although the flame looked all right, we were getting CO in the waste gases. I had thought the experience

of any melting-shop manager would enable him to detect CO in the waste gases, but there was something different happening here. We could not increase the air supply to any great extent, so we had to reduce the gas-port area. We did this gradually, and eventually finished up with a gas/air ratio giving CO_2 readings of $17\frac{1}{2}\%$ or 18% , which we thought ideal, while the port pressure was about 1.1 or 1.2 in. water-gauge, which I believe is exceptionally high. We think that we have something here, which furnace performance confirms; but we are going to proceed further on these lines before we can be fully satisfied.

Mr. THRING (in reply): With regard to stratification in the furnace, I think that Dr. Leckie's suggestion of putting a little air in at the top is well worth looking into. If we could use a brick which could stand more temperature it would be an improvement, but until we have conditions such that we can get the roof up to its limiting temperature very quickly and keep it there, there is no need to worry about methods of running at still higher temperatures; the first objective is to get that limiting temperature quickly and keep it, and then, so long as silica bricks have to be used, the stratification may remain a useful way of increasing output, although at the expense of full economy.

Mr. Wright referred to the absorptivity of the charge. That is brought into the theory, and it is shown that to reduce the working temperature of the slag surface for a given steel temperature is one of the most effective ways of increasing output. Whether we do that by getting the steel to move through the slag more violently or by using a thinner slag, it is possible to get very considerable advantages, and one of the major points of the theory is the emphasis which it lays on that fact.

As far as the question of correlating output with thermal efficiency, raised by Dr. Sarjant, is concerned, we could not do that; we had to work more or less with the conditions as they were, and we were not in a position to run casts deliberately with different gas consumptions, so that we could not draw a characteristic curve of gas input and thermal efficiency of the kind that Dr. Leckie has used. To produce those curves is of great value; but we can still draw definite conclusions as to the most promising line to improve both output and thermal efficiency, even from the results which we did get. That is the general answer to all these points—that it is possible to draw fairly clear conclusions about what to do in the future, in spite of any criticisms which may be quite rightly levelled at the actual experiments; and I think that is where the use of a theoretical background does strengthen the work very considerably.

Mr. Wright referred to the question of opening up of the surface of the slag, and of that cooling

the flame. I agree with him; personally, I think that is the cause of the critical period. There is a time when the steel surface temperature is low, and it is then that plenty of gas, and good quality gas, is wanted, as has been mentioned. That, I think, is the explanation of the critical period, rather than the one, given by Dr. Leckie, of time-lag in the regenerators; but that suggestion by Dr. Leckie could probably be answered by a more detailed analysis of the results, and I hope we shall be able to do that.

Finally, there is the question of the calorific value of the producer gas. The measurements were made on an instrument in which the sample was cooled and all the tar and water-vapour taken out, and therefore they do not correspond to the gas as burnt. An improved instrument which would read the calorific value of the gas as burnt or its radiating power under standard conditions burnt in a special apparatus would be a great advantage, and perhaps it will be possible to develop such an instrument.

CORRESPONDENCE.

Mr. G. A. V. RUSSELL (Messrs. Dorman, Long and Co., Ltd., Middlesbrough) wrote: The authors have earned the gratitude of all those who are interested in steel-furnace design and operation for their painstaking investigatory work and for the ingenuity they have displayed in devising apparatus and procedures. The Report is of special interest to the writer as he was largely responsible for the design and installation of one of the furnaces used in their tests—the *S* furnace—and is pleased to note that, in general, the performance of this furnace was favourable, despite certain restrictions and handicaps which surrounded its design.

In the introductory section of the Report, dealing with the present state of port design, it is somewhat surprising that no illustration is given of the usual solid block with single overhead air port, which, on account of the wide vogue this type has enjoyed, and still does, may be regarded as the normal European producer-gas port construction, whereas the type shown in Fig. 5(a) was developed at Templeborough from the former design. The writer knows of many furnaces with this simple type of block which give high rates of output per square foot of hearth area, and it satisfies a requirement adumbrated by the authors, that the main roof area of a furnace should be as nearly as possible the same as its hearth area.

A factor which indirectly influences the efficiency of given flame conditions is the rate of heat loss through the furnace bottom. This loss is somewhat less in the *S* furnace than for the other two furnaces tested, a point which may tend to increase the apparent heat-transmission efficiency of the first-mentioned furnace and be a contributory factor in the somewhat lower recuperative efficiency of the regenerative system.

In connection with the authors' ingenious heat-flow meter, it would be interesting to have their opinion as to the relative advantages of this method, as compared with the measurement of the radiating power of the flame or its emissivity, which forms the basis of the good work carried out by Fisher in America. The Fisher apparatus appears considerably simpler to use for routine

checking of flame characteristics, but its value would seem to depend on how far the measurement of emissivity alone can be regarded as giving a quantitative idea of the value of an open-hearth flame. The writer would think that there is little to choose between the two methods when measurements are desired after the charge is virtually melted, but he is not so certain whether the Fisher apparatus would provide means of determining flame suitability when melting down a cold-metal charge, or a low-iron hot-metal heat.

The authors' general conclusions would be of greater interest if they could indicate as to how these would be specifically applied in the three furnaces tested.

Ir. J. E. DE GRAAF (Ijmuiden, Holland) wrote: Being fully aware, through his own experience, of the difficulties which have to be surmounted in experiments on open-hearth furnaces, the writer gladly takes this opportunity to congratulate Dr. Chesters, Mr. Thring, and their collaborators, on a fine piece of research.

There is however some reason to be cautious about optical measurements, and perhaps radiation measurements in general, in the open-hearth furnace. It is of course a well-known fact that dust must be present in the hearth, *e.g.*, because the dust that appears in the checkers must at least partly have been dust in the hearth. Moreover the writer found that the "flames" which appear at the top of the doors or above the checkers often possess no combustibles, so that the "flames" were attributed to incandescent dust. That this dust can have influence on optical measurements can be assumed. It has been possible to show this directly under favourable conditions. The influence varies with the conditions in the furnace and with the type of instrument used; values of this influence have been found to be between 20° and 120° C. in optical temperature measurements. It cannot be predicted in general which type of instrument is least sensitive, as often the colour pyrometer is less influenced, compared with total-radiation or disappearing-filament types, but

sometimes the reverse is true. This influence of dust may partly explain the variations in the optical and radiation measurements in the Report. It might also be a reason why a heat-flow meter fitted to the front wall could show less correlation with the radiation of the flame than a heat-flow meter between flame and bath. Some indications were obtained in the writer's experiments that the amount of dust decreases at the end of a heat, but this decrease was too slight to make optical measurements entirely reliable, even during the final stages of the heat. Reflection, too, as is well known, is not negligible and therefore also can be a cause of faulty measurements. This was found, *e.g.*, in roof pyrometry.

The roof pressure has been investigated by the present writer as a controlling factor of air in-leakage under many circumstances. Certainly under many conditions the roof pressure proved to have a major influence, but under other conditions the influence was much less, and sometimes

TABLE B.—Water-Cooling Losses in C.H.U./min.

Furnace.	Single-Door Average.	Single-Port Average.	Jamb Coolers of a Single Door.	Arch Cooler of a Single Door.	Door Itself.
Ijmuiden	Total 11,250	6500	2800	5100	3350
<i>S</i> . . .	5920	6600
<i>K</i> . . .	8430	5850

even only slight. This could be correlated to the position of the flame in the furnace, which usually changes during a campaign owing to wear of the ports. This, too, is responsible for the changes in the roof pressure necessary to obtain the same amount of flames at the doors. As the latter is largely the criterion for maximum roof pressure, instructions were issued to the furnace crews to adjust the draught so as to obtain the maximum allowable amount of flames at the doors, rather than keep the roof pressure at some fixed value.

As regards the optimum total amount of air used, we determined the total amount of heat (chemical and sensible) in the waste gases as a function of the oxygen content of the gases. It was found that the loss in the waste gases had a shallow minimum between 2 and 3% of oxygen in our circumstances. The amount of combustion air is adjusted so that this concentration is reached. Of course, it is necessary to keep in-leaking air as low as possible as the oxygen concentration is not the only criterion for best firing conditions.

With respect to heat balances, it is perhaps worth while to record for comparison purposes some of the writer's results on five-door Venturi furnaces of about 90 tons tapping capacity.

Table B contains data of the Ijmuiden furnaces and some of the data of the Report under consideration.

As a cooling element of the doors, the welded box frame of *S* and *K* furnaces is equivalent to the separate jamb coolers plus the arch cooler of the Ijmuiden furnaces. It is not quite clear from the Report whether the doors themselves were water-cooled in *S* and *K* furnaces and whether the losses thereof are included in the total figures of

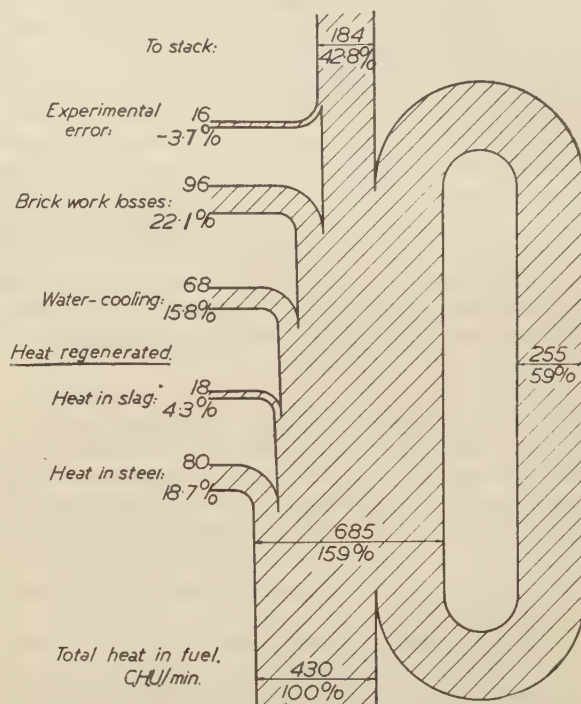


FIG. F.—Graphical Representation of Heat Balance. Average of nine heats.

the doors. The figures for the Ijmuiden doors show that an improved construction for the arch cooling is desirable; this is being tried now. The port cooling of the Ijmuiden furnaces is identical with that of *S* furnace. The figures given are an average of many heats, using for each heat the average around which the momentary loss fluctuates with flame direction (quick fluctuations) and with the general change of temperature of the furnace during a heat (slow fluctuations). The slow fluctuations are about -7% (from shortly after starting to charge) to $+7\%$ (at the end of the heat).

The losses through the brickwork were estimated with the aid of extensive measurements of surface temperatures of the brickwork all over the furnace, in combination with coefficients for specific heat loss as a function of temperature and depending on the direction of radiation from the brick surface. The coefficients were determined partly from sources in the literature and amplified by our

own experiments. Detailed comparison with the brickwork-loss data of the Report is somewhat difficult because of different furnace constructions. Total heat in gases, *i.e.*, preheat in gas and air, flue-gas heat, &c., was determined with suction pyrometers and gas analysis (tar of producer gas included). The suction pyrometers had a slightly more elaborate head than that shown in the Report, as the head consisted of a cylinder of mortar through which numerable small holes were pierced parallel to the axis, leaving very thin walls between them, after which the cylinder was fired.

Fig. F shows the heat balance in graphical form as an average of 9 individual heat balances which were distributed over a few campaigns, in such a way that their average gives a fairly accurate picture for a whole campaign. It is felt that this balance can be very much improved upon as regards efficiency as the experiments were made during the occupation of Holland, when information only was looked for and actual immediate improvement was avoided entirely. Nevertheless, the heat balance has shown definite data for all losses and heat distribution.

Mr. F. KENNEDY (Messrs. Dorman, Long & Co., Ltd., Middlesbrough) wrote: I should firstly like to congratulate the authors on the record of a magnificent piece of work which will undoubtedly be consulted as a standard reference for many years to come. The Report covers so much ground that the discussion on it could probably be continued indefinitely.

From the point of view of our own local practice, I am rather surprised that the authors have not included in their list of typical ports that which may be described as the Port Kembla type. This district had the largest number of Hoesch furnaces in the country, but they have all now been replaced by furnaces with the Port Kembla type of block and this conversion has resulted in a reduction in the fuel consumption per ton of ingot of more than two million B.Th.U.'s, *i.e.*, from above seven million to below five million. If the two types of furnaces had been instrumented in a similar fashion to the test furnaces described by the authors, I am certain that very interesting data would have been obtained, giving further confirmation of the views expressed by the authors regarding effect of flame temperature on rate of heat absorption by the bath. The disadvantage of the Hoesch port was that the mixing of cold, high-velocity gas with the highly preheated air at low velocity commenced intense combustion with a high flame temperature, which had the effect of quickly burning down the "relieving arch," and in order to obtain a reasonable life of this arch, extensive water-cooling was necessary which reduced the flame temperature. The gas system and the furnaces were so arranged that

ample fuel input into the furnace was always possible and thus, although the furnace output did not suffer seriously from the reduction in maximum flame temperature, the furnace output was obtained only by pumping in additional quantities of heat.

Further, with the Hoesch type of port it was considered advisable to introduce the carburetting agent into the gas stream at an angle, and there was always the danger of impingement on the side walls of the furnace; with the Port Kembla type of burner, the carburetting agent is introduced into the middle of the gas stream and impingement on the side walls is completely eliminated.

In view of the data which Dr. Chesters will have now collected from these tests, his views on roof insulation are requested.

Fig. 26, showing the method of mounting the roof-temperature equipment, appears, as the authors state, rather cumbersome, and I should like to have their views regarding alternative types which could be fitted as part of the furnace system and would not leave an opening in the furnace wall for radiation loss and air infiltration.

I am not clear whether the statement on p. 67, that a 10% increase in the radiant heat transfer is obtained with an increase of 10° C. in the flame temperature, is purely a theoretical calculation, or whether experimental evidence confirming this was collected during the test.

A temperature of 1680° C. is mentioned as the melting point for the silica brickwork and one 30° C. lower, *viz.*, 1650° C., is mentioned as the safe working point; is it not probable that with different types of practice and charges, varying amounts of oxide or lime penetration of the brick may occur which could result in quite a variation at different plants?

On p. 78 it is stated that some heats were worked with no variation in gas flow from the beginning to the end of a heat; this is rather surprising, unless we are to understand that there were physical difficulties in increasing the gas flow as, during melting, the furnace heat requirements are usually decidedly higher than in the refining period.

The conversion of the Mono CO₂ and CO recorder to a CO₂ and oxygen recorder was very ingenious and I should like to know whether arrangements have been made to put an instrument of this type into commercial production.

On p. 91 it is stated that there were indications that roof wear increases with the life of the checkers. Is this correctly expressed and are there not likely to be other variables affecting the roof wear besides life of checkers? I have in mind particularly the fact that usually if the checkers are getting old, the roof itself and other parts of the furnace are likely to be old, so that any increased wear of the roof is not necessarily due to the increased life of the checkers; in fact, it

is the general opinion that with increased life of checkers the preheat and quantity of fluid passing are both likely to be decreased.

The mention on p. 142 of the multi-point probe covers another "grand tool" which the authors have utilized. I myself am in complete agreement with the contention of the authors that, with producer gas, quick mixing of the gas and air are highly desirable, but, on the other hand, one frequently meets open-hearth operators and managers who, in practice, prefer to have the flame reaching from port to port. I should like to hear further from the authors on this point.

In view of the marked effect of the fall in preheat temperatures during reversal, I should like to have the authors' opinions regarding what they consider the optimum reversal cycles.

The fuel consumption expressed in millions of B.Th.U.'s per ton of steel, shown on p. 156, ignores both the sensible heat and the tar content of the gas. The sum of these two factors would be at least another 35 B.Th.U./cu. ft., which would increase the figures as expressed by the authors by at least 24%, but in our own organization we also consider that the gasification of the coal is part of the process and therefore the losses resulting in the producer should also be included. If allowance for these two factors is made, the B.Th.U. consumption per ton of steel will probably be 7.12×10^6 B.Th.U./ton of steel. The tabulations also show that the slowest working furnace has the lowest fuel consumption. This is decidedly different from our experience, as we almost invariably find that the easiest way to improve the fuel consumption on any of our open-hearth furnaces is to drive for an increased output.

I should like the authors' views on the value of automatic control of the furnace pressure as compared with hand control.

I suggest that it would have been preferable to have installed the gas calorimeters in the gas uptake so that the effect of the reversible reactions which can take place in the gases on their passage through the regenerators would have been taken into account. The fluctuations in calorific value and combustibles which can occur under some conditions are very extensive and in extreme cases I have found a change of between 15 and 25 B.Th.U./cu. ft. It is true that the location of the calorimeter at the producers is essential as a guide to the operators regarding the producer operation and therefore my suggestion would have increased by two the very large number of instruments employed by the authors.

The statement on p. 158 that the highest air preheat was obtained from the old checkers on the K furnace, is difficult to explain in view of the fall in heat transfer claimed to be obtained from old, dirty, glazed surfaces.

Automatic reversal control on waste-gas temperatures is mentioned on p. 161. Which particular temperature or temperature difference would the authors recommend to be taken as the impulse device to set the control mechanism in operation?

Mr. Thring, in his concluding remarks, stated that if we were using a carburetted flame there were advantages in reducing the amount of carburetting agent in order to lower the roof temperature; this is not in accord with my own ideas. The addition of the small amount of carburetting agent increases the rate of heat transferred to the bath very appreciably and therefore I contend that in the interests of fuel economy and good furnace operation, the rate of heat input in the gas should be reduced. This would attain the object of continuing the transfer of the maximum amount of heat to the bath at the minimum expense of fuel.

I should once again like to express my thanks to the authors and their team of workers for this Report. The only fear I have is that they have reported their results in such detail that many who would benefit by study of the work undertaken, will be deterred by the amount of information supplied, and thus its great value will not be thoroughly appreciated by the very people to whom it should be of the greatest value.

I should like to repeat in different language Mr. Thring's concluding remarks; *i.e.*, the authors state that after making due allowance for the standard type of charge used, the utilization of the instrument readings cut down the working time per charge by one to two hours, but I would emphasize that the instrumentation which they consider of the greatest value can be reduced to four primary instruments to be used for the following purposes:

- (1) Roof-temperature control.
- (2) Furnace-pressure control.
- (3) and (4) Air/gas ratio control, which involves the measurement of both air and gas.

The other instruments and readings which were used are mainly for the use of specialists when wishing to examine the furnace performance and to compare one type of construction with another.

Dr. A. H. LECKIE (The British Iron and Steel Research Association, London) wrote: Mr. Pearson has suggested in the discussion that our views on air/gas ratio had changed since the publication of the 1944 paper on the correlation of open-hearth data.* No doubt Mr. Pearson is referring to Fig. 7 of that paper, in which it is suggested that high thermal efficiencies are obtained in certain cases with high air/gas ratios of 2:1 or more. Attention should be drawn, however, to the text

* A. H. Leckie, *Journal of The Iron and Steel Institute*, 1944, No. I., p. 419 P.

accompanying this figure in which it is stated that "care must be taken not to interpret this too rigidly, as a low air/gas ratio, in furnaces where the air flow does not vary much, may simply mean that the gas rate is higher than usual."

This has, in fact, been found to be the case; in the furnaces illustrated in Fig. 7 of the 1944 paper, the air flow did not vary very much; hence, in separating out the heats with low and high air/gas ratios for statistical analysis, what in fact was obtained was a grouping with high and low gas flow, respectively. Now, it is a well-known fact that the thermal efficiency of an open-hearth furnace under production conditions tends to increase as the gas rate decreases (*see* Figs. 1, 3, 4, and 5 of the 1944 paper *); an extreme case of this would occur at a very low gas rate just sufficient to melt a charge. In such circumstances the charge would be at a low temperature during a substantial period of the heat, thus giving a high heat transfer and a high thermal efficiency (calculated as a percentage of the heat in the fuel transferred to steel and slag). Hence the high thermal efficiencies with high air/gas ratios found in 1944 were mainly due to the low gas rates which were associated with the high air/gas ratios in these particular furnaces, and the warning given in the qualifying statement attached to the graphs has been justified.

Experiments at the Shelton experimental furnace have shown that strict control of the air/gas ratio to a value approaching theoretical is essential to secure highest heat transfer to the charge (as distinct from thermal efficiency), thus we are in good agreement with the results of the Templeborough trials and with Mr. Pearson. Nevertheless, in production furnaces, it is frequently found that excess air is necessary to obtain satisfactory combustion—this is a symptom of bad port design and this has been confirmed at the experimental furnace.

Referring again to statistical analysis, and the 1944 paper, on p. 21 of the present Report, Miss Boswell and Mr. Thring state that "one definite conclusion is that the number of the cast in the week has in no case any significant effect on the performance of the furnace." It should be made clear that this conclusion does not apply to all furnaces, and whilst this may be the case at Templeborough, reference to Fig. 8 of the 1944 paper shows that the week-end shut-down has a real effect on some furnaces; the effect in the case of the 40-ton furnace and the 60-ton furnace is statistically significant; the 80-ton furnace (at Shelton) is an example of a furnace which is not seriously affected in this way.

Mr. J. CHAPMAN and Mr. G. LOMAS (Messrs. Steel, Peech & Tozer) wrote: It is emphasized in

* Thring and Reber have shown that the curve *RR'* in Fig. 1 of the 1944 paper, if drawn back at lower heat inputs, would fall again. (*See Journal of the Institute of Fuel*, 1945, vol. 19, No. 104, p. 12.)

the Report that the figures given for furnace roof pressures were relative but not absolute.

It was realized early in the trials that the recorded values would be low, owing to the fact that the vertical part of the pipe connecting the tapping to the recorder was close to the furnace, but time did not allow for any alternative layout.

Spot readings taken on the roof during the trials confirmed the belief that the recorded figures were low, and the error was in the region of 0.04 to 0.05 in. water-gauge. This figure was checked at a subsequent and more convenient time to determine whether the error was constant.

On four furnaces in this same shop the results were as follows:

(1) A second recorder was located on the roof and connected into the short vertical pipe which rises from the roof tapping, without disconnecting the instrument in the cabin. Continuous records for 36 hr. of the two instruments were compared and showed maximum variations of 0.04 to 0.05 in. water-gauge.

(2) The difference of pressure at the top and bottom of the vertical pipeline beside the furnace was recorded and found to remain constant at 0.045 in. water-gauge over a long period.

Mr. T. F. PEARSON (Messrs. Colvilles, Ltd.) wrote: It is hard to comment on the Report of Dr. Chesters and Mr. Thring and their colleagues, since the field covered is so extensive. I feel it would have been better had it been issued in sections at intervals. The record presented, however, is an admirable example of the conclusions which can be reached when a mass attack is made on such a complex problem as that presented by the open-hearth furnace, and Dr. Chesters and his colleagues are to be complimented.

The two most important points which appear to emerge are: The necessity for pressure control within the laboratory, and temperature control at some safe maximum to ensure that maximum heat transfer is always taking place. Although no theoretical objections exist, the practical difficulties in each case are appreciable and have not been entirely surmounted up to the present. It is possible by increasing the pressure within the laboratory (by cutting down draught outgoing) to maintain a high temperature with some particular gas-plus-air input, and at the same time, to fail to put in thermal energy at a sufficiently high rate to ensure maximum rate of steel output. For this reason a compromise becomes necessary, rather than a rigid theoretical requirement, and it is the evolution of practice to this point which develops the fastest speed. It is obvious, however, that reliable

facilities for measurement, beyond those at present normally incorporated in a furnace, are necessary, and will have to be evolved as standard equipment for future furnaces. This improved ability to measure, coupled with the use of fuels (such as oil) containing less inert material, is responsible for the faster working rates now coming to notice.

I have been interested in the progress of the heat-flow meter. Its elaborateness, however, prevents a wider adoption and I have tried to imagine how the flame can be improved, with existing controls, to give a greater transmission, supposing a low reading is actually obtained in the furnace.

From this point of view I believe that more would be learned by putting a flame inside a heat-flow meter, *i.e.*, what we require is a comprehensive

study of radiation characteristics under closely controlled conditions to discover the significance of mixing, and the effect of falling off in preheat with time. Until this is done we shall not be able to define our ultimate requirements as to ideal control.

I am interested in the actual coal consumptions pertaining to the trials, but find in the heat balance, Table LXXIV., that there is no mention of tar in the gas, the calorific value used in the calculations being that of clean gas. Since the tar content should be equivalent to an additional 15 B.Th.U./cu. ft., approximately, and since no mention is made of "hot gas efficiency," I presume that the gross coal consumption was of the order of 5 cwt./ton of steel, *i.e.*, $51.5 \times (165/150) \times (100/80)$ therms/ton.

AUTHORS' REPLIES.

Dr. CHESTERS wrote in reply: Replying to Dr. Leckie, we should be very surprised if the critical period which we observed on certain casts had anything to do with the cooling of the checkers by the scrap charged in the furnace. If this was so, we should expect the effect in every cast, whereas in point of fact it was found only in some of them. We are strongly of the opinion that the drop in roof temperature during this critical period is due to the greater ability of the charge to absorb heat. Further work is now being carried out to see whether we can find out just what condition it is which is responsible for this heat absorption, which has, we understand, been observed not only on gas-fired furnaces but on some of the best oil-fired furnaces.

We are inclined to agree with Dr. Leckie that it would be better to measure preheat by means of radiation pyrometers sighted on the uptake walls or preferably by some kind of suction pyrometry at stage level. General information gained as a result of the publication of this Report is all in line with our suggestion that a substantial part of the regenerated heat is picked up in the slag pockets, uptakes, &c., rather than in the checkers.

Mr. Wright refers to a roof temperature of 1630° C. being used in the experiments. It is true that we were not always able to get a temperature of 1650° C., but this was the maximum safe temperature fixed and would always have been attained if the necessary heat had been available. Given better control, and we are now striving to improve the accuracy of our own equipment, higher control levels should be possible, though we are still very dubious about Mr. Robertson's 1680° C.

We are very grateful to Mr. Russell for his friendly comments on our Report, and are glad that the furnace which he designed showed up so

well in the tests. We have studied Fisher's method of measuring heat flow, and although we are in full agreement with this as a practical measure for increasing efficiency, we are not too happy about the assumptions made. The flame radiation measured at the incoming end includes both flame and bath. We think that flame plus brickwork would be better, though admittedly more difficult to attain. At the outgoing end, the reading on a radiation pyrometer sighted through the roof on to the bath is employed as a rough measure of the roof temperature. We feel that even though there is no flame left in this region, it is dangerous to assume that the surface of the slag is at the same temperature as the surface of the roof.

With regard to Mr. Russell's query as to how the results are to be applied to the particular furnaces considered, we would state that we are at present designing a conventional furnace, making use of the information obtained in our researches, and that when the drawing has been approved we shall attempt to apply the information both to existing furnaces and to the erection of any new furnaces we may wish to build. We do, however, consider that models represent an essential intermediate stage, and Mr. Russell will be interested to know that water models, both of *K* and *S* furnaces, are now under construction and should be undergoing test in the very near future.

In reply to Ir. J. E. de Graaf's remarks, we would state that the doors themselves on *K* and *S* furnaces were not water-cooled.

Replying to Mr. Kennedy, our feeling with regard to roof insulation is that it is of very doubtful value. Provided that the roof pyrometry is satisfactory, there is no reason why an insulated roof should not be operated without its

being melted, but it is now well-known that a slight overheat on an insulated roof will do far more damage than on an uninsulated roof, since a given amount of heat will raise a far greater thickness of brickwork above the critical temperature. Since periodical overheats are almost unavoidable when there is any real drive for production, we consider that any savings that may accrue are more than offset by the risk of roof failures.

We are experimenting with several new types of roof-temperature equipment, including the photo-cell arrangement devised by Land, and we have also modified the supporting gear on the instrument described in the Report. The new arrangement is lighter and permits of easier adjustment; it also allows the instrument to be swung completely out of position when a calibration check is being made.

We have examined the various zones in silica bricks from different sources, and consider that the maximum safe temperature will not differ very greatly according to whether the furnace is acid or basic, since fluxes arriving on the surface are absorbed by the brick, and the surface composition and melting point are much the same from one furnace to another.

Mr. Kennedy is right in assuming that there were physical difficulties in increasing the gas flow during the trials. We just had not the gas available that we should like to have had, although, as already stated, this position is being remedied. We too were surprised to find that the fastest furnace was least efficient on fuel, though we have heard of other examples since, *e.g.*, certain all-basic furnaces have been found to consume more oil per ton in spite of much bigger outputs.

The statement that the highest air preheat was obtained from the oldest checkers is perhaps misleading, because this checker was so blocked that the air volume was sub-normal. If the air volume had been normal, then the preheat would undoubtedly not have been so high. We have no definite information as to whether it is better to reverse on time or on temperature or on some particular temperature differential, but we feel that any control arrangement should enable the operator to switch on to manual control or various types of automatic control, as desired. This is the practice in certain of the latest American plants.

The answer to Mr. Pearson's question about the desirability of putting the flame inside the heat-flow meter instead of the heat-flow meter in the flame should really be given by Dr. Leckie. Surely, that is what he has been attempting to do in his experiments at Shelton. A model furnace of this type, operated with different kinds of fuel, should show up such things as changes in calorific value, luminosity, &c., in the manner described

by Mr. Pearson, and in a more directly applicable fashion than would be expected from a simple water-cooled calorimeter surrounding the flame.

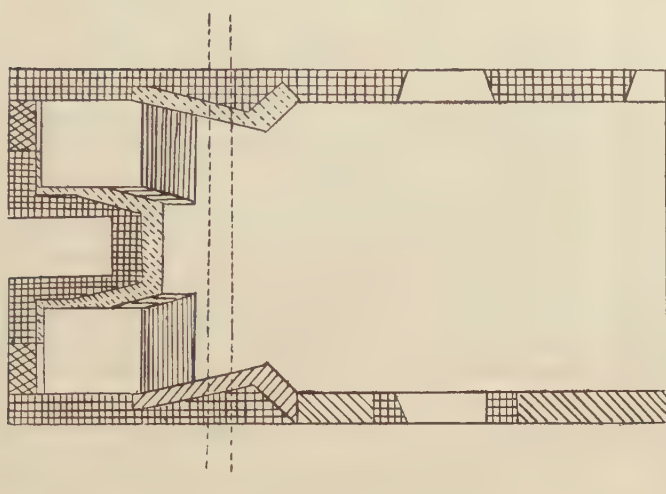
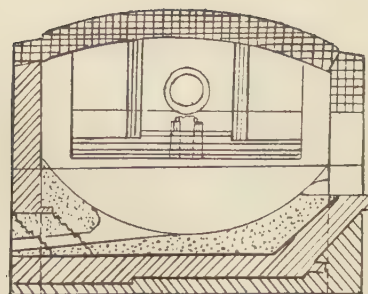
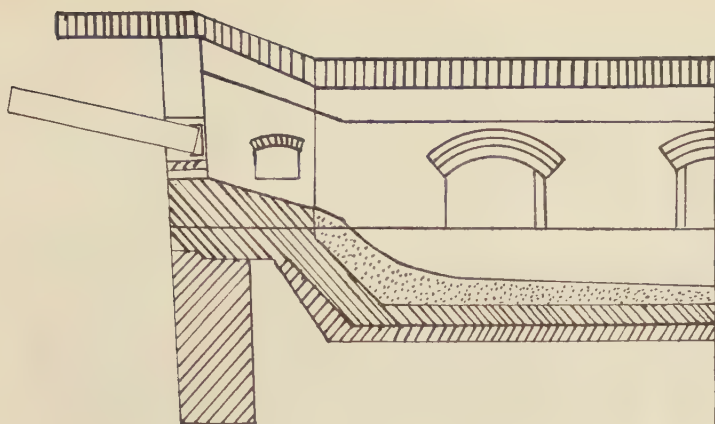
In conclusion, we should like to take this opportunity of thanking all the contributors to the discussion, on behalf of both The United Steel Companies' Open-Hearth Advisory Committee and The British Coal Utilisation Research Association, for the extremely kind way in which they have received our Report. We hope that it will not be very long before we have further information to report which will help to "bridge the gap" between the survey we have made and the everyday job of designing and operating furnaces.

Mr. THRING wrote in reply: Replying to Ir. de Graaf, the comment about the necessity to be cautious in regard to optical measurements would apply very strongly if these measurements were intended to be regarded as measurements of temperature. Under such conditions dust can give a considerable error. Since, however, our actual measurements were measurements of total radiation it does not matter whether this radiation comes from gases, walls, or flames, and it is not, therefore, necessary to apply any correction to the readings.

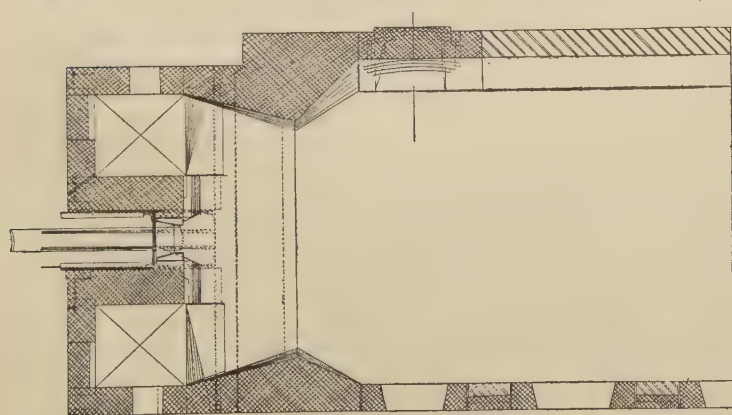
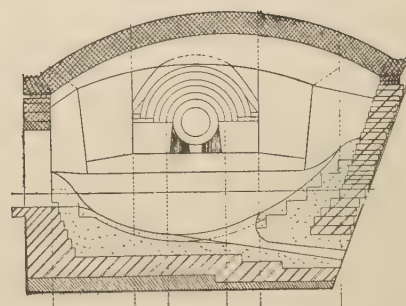
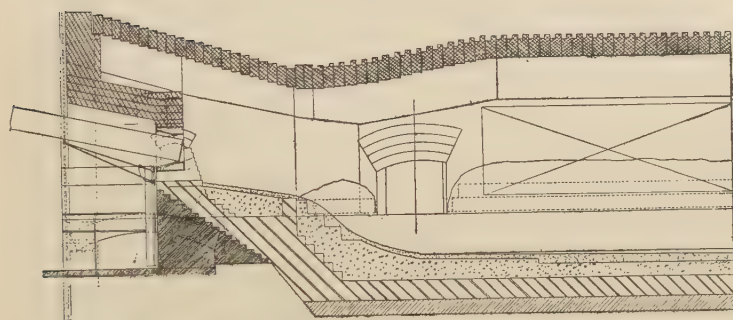
In reply to Mr. Kennedy, the inclusion of the Port Kembla coke-oven gas burner into the summary of port designs is certainly a very valuable addition and a figure of Mr. Kennedy's particular form of the Port Kembla design is shown in Fig. G.

The statement on p. 67 of the Report is as it stands purely a theoretical conclusion, but the trials all indicate that this particular conclusion is certainly not far out.

As regards the Mono CO₂ and oxygen recorder, steps are being taken to put this instrument into commercial production. So far as the flame length is concerned, one of the most convincing conclusions from the trials is that producer-gas flames certainly tend to be too long and that the shorter the flame is, the better, provided that it is not so short that it is causing serious refractory trouble at the ingoing end, a condition which is very rarely, if ever, achieved with producer gas and which does not even seem to be frequently achieved with oil. There would appear to be no doubt that the optimum reversal cycle would be shorter than the 15 min. which occurred in the trials, both from the point of view of uniformity of preheat and maximum efficiency, and hence reduced fuel consumption. There is no doubt in our opinion that automatic control of the furnace pressure is preferable to hand control, provided that it is carried out in a manner which allows safeguards against various difficulties which are automatically allowed for in hand operation.



(a) *R* furnace.



(b) *M* furnace.

FIG. G.—Port Kembla Burner as Applied at the Works of Messrs. Dorman, Long and Co., Ltd.

As regards carburetted flames, the conclusion that it is better to cut the carburetting addition rather than the gas quantity when the roof reaches the limiting temperature, applies only under very restricted conditions where it is desired to increase the rate of heat input to the bath after the roof has already reached its safe limiting temperature, even though this increase is obtained at the expense of fuel economy. Under all other conditions, such as where the roof has not yet reached its limiting temperature, where a better refractory is available, where fuel economy is of greater importance than output, or where the bath has already reached the required temperature, this conclusion does not apply and it is better to cut the gas rather than the carburetting additions.

Replying to Mr. Pearson on the question of the elaborateness of the heat-flow meter, it is considered this instrument is not too elaborate for every melting shop to make frequent use of at least one such instrument. Nevertheless, there is no doubt that the study of a flame under laboratory conditions can give results of considerable interest. Dr. Leckie's experimental furnace at Shelton represents a very valuable step in this direction and it is hoped to build a laboratory flame furnace at the B.I.S.R.A. Physics Depart-

ment at Battersea for a further study of this problem.

The assumption made by Mr. Pearson as to tar in the gas is correct.

Mr. BAULK wrote in reply: With reference to Mr. G. A. V. Russell's query about the relative advantages of the heat-flow meter and A. J. Fisher's method of measuring flame radiating power, it was fully realized that his method was much simpler for routine measurements, and for this reason the so-called front-wall pyrometers were developed. The heat-flow meter, however, has the advantage that it can be made to "see" exactly the same radiating surfaces as the steel at any point over the bath area. Also, it measures total radiation, whereas Fisher's instrument and the front-wall pyrometers measure only that radiation transmitted by a quartz window.

It should, however, be emphasized that the heat-flow meter is primarily a research instrument, and is not intended for routine works use. The front-wall pyrometers give a convenient substitute for regulating furnace operation, and if used in conjunction with occasional readings with the heat-flow meter, should prove a valuable control instrument.

THIRD REPORT ON REFRACTORY MATERIALS.

BY THE JOINT REFRACTORIES RESEARCH COMMITTEE OF THE BRITISH IRON AND STEEL RESEARCH ASSOCIATION AND THE BRITISH REFRACTORIES RESEARCH ASSOCIATION.

THIS Report is published as Special Report No. 32. It was included in the programme of papers presented at the Autumn Meeting of The Iron and Steel Institute, held in London, at The Institution of Civil Engineers, on 13th and 14th November, 1946.

SYNOPSIS.

The Third Report on Refractory Materials is divided into six Sections. The first, Section A, is of an introductory nature and includes a Foreword by R. A. Hacking, Chairman of the Open-Hearth Refractories Joint Panel, and A. T. Green, Director of Research, British Refractories Research Association, and the Constitution of the Committees and Panels as in 1945.

Section B is devoted to chrome ore and contains five papers. In the first, by A. E. Dodd and A. T. Green, the hypotheses which have been put forward to account for the formation of chrome-ore bodies are briefly reviewed. The ore is now considered to be either magmatic or hydrothermal in origin. The geological literature on the world sources of chrome ore is examined, and the mineral associations and probable mode of genesis of each deposit are described. The second paper, by W. Hugill and A. T. Green, deals with the constitution of chrome ores and describes the analysis of seventeen samples of chrome ores from nine localities. The composition, refractive index, and specific gravity of the separated chrome grains have been determined and the proportions of chrome grains and gangue in each sample calculated. The third part of Section B constitutes an investigation of chrome ores, by G. R. Rigby, G. H. B. Lovell, and A. T. Green, and the results are presented under the following five headings: "The Action of Reducing Gases on a Number of Ores," "The Effect of the Constitution of the Chrome Grains on the Action of Reducing Gases," "The Properties of the Spinels: Chromite and Hercynite," "The Action of Iron Oxides on Spinels and Chrome Products," and "Volume Changes Occurring when Binary Mixtures of Spinels are Heated between 800° and 1,400° C." J. R. Rait, in paper No. 4 presents an X-ray investigation into the constitution of chrome ores; X-ray photographs are included of chrome ores both in the raw state and after mixing under oxidizing and reducing conditions. Similar photographs have been obtained of the spinels $\text{MgO} \cdot \text{Al}_2\text{O}_3$, $\text{MgO} \cdot \text{Cr}_2\text{O}_3$, $\text{FeO} \cdot \text{Al}_2\text{O}_3$, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, and of a range

of their solid solutions with each other. The solid solutions of Al_2O_3 , Cr_2O_3 , and Fe_2O_3 have likewise been examined. A paper by N. E. Dobbins and W. J. Rees on the effect of precalcination on friable chrome ores concludes Section B. Various size-gradings of a Transvaal chrome ore which develops friability on firing were calcined for two hours at 1,550° C. with different proportions of (a) serpentine (b) serpentine and magnesite, (c) dolomite, (d) stabilized dolomite, and (e) lime, in a laboratory gas-fired furnace. The sieve analyses of the crushed products, the expansion or contraction on refiring the clinker with finely ground magnesite, and the iron oxide bursting expansion of the resultant products have been determined.

Section C deals with investigations on other steel-furnace refractories. The first part is by N. E. Dobbins and W. J. Rees and deals with some observations on the draining of slags at high temperature. It is concluded that this investigation opens up a large field for research, but that much further work must be carried out before its importance can be fully determined. Of immediate importance, however, is the application of the results of this investigation to laboratory slagging tests as conducted by the usual methods; and in particular, the extent of the error introduced and the interpretation of the results of these tests. The second part, by G. R. Rigby, G. H. B. Lovell, and A. T. Green describes the petrological features of basic bricks which have been in service in the back walls of basic open-hearth furnaces. The bricks include chrome-magnesite, chrome-magnesite-olivine, and magnesite-olivine products. The investigation on other steel-furnace refractories is continued with a paper by N. E. Dobbins and W. J. Rees on the fusion relations of the ternary system magnesite/calcined-dolomite/basic-slag, and of other basic refractory materials with basic open-hearth slag. In the concluding paper of Section C, G. R. Rigby and A. T. Green describe a petrological examination of magnesite blocks taken from the lining of an inactive metal-mixer. The reactions at the hot face appeared to be similar to those occurring in magnesite-olivine bricks when used in the back walls of open-hearth furnaces.

In Section D two papers are devoted to casting-pit refractories. The first, by A. E. Dodd and A. T. Green, records some observations on ladle linings used in the casting of basic open-hearth steel. Variations in the factors affecting ladle life have been studied and correlated with the wear of the ladle lining. The second paper, prepared by J. H. Chesters, A. E. Dodd, J. R. Priestley, and J. R. Rait, constitutes a report of the Casting-Pit Refractories Sub-Committee of the Open-Hearth Refractories Joint Panel. Subjects discussed are the standardization of casting-pit refractories, investigations on runner bricks, the question of refractories as a source of non-metallic inclusions in steel, and some experiments on the spalling resistance of casting-pit refractories.

In Section E, dealing with electric-steel-furnace refractories, a report is made on the roofs of electric-arc steelmaking furnaces by the Electric-Furnace Refractories Sub-Committee of the Open-Hearth Refractories Joint Panel. In this paper, with a Foreword by R. J. Sarjant and A. T. Green, a survey is made of the design and life of the roofs of seventeen electric-arc steel furnaces; relevant features of operation are also tabulated.

Finally, in Section F, is given a summary of other published work of the British Refractories Research Association which is of interest to the iron and steel industry. Special attention has been given to basic refractories, silica refractories, and the action of slags and gases on refractory materials.

THE DEVELOPMENT OF MONOLITHIC DOLOMITE LININGS.

BY THE TECHNICAL PANEL OF THE BASIC FURNACE LININGS COMMITTEE.

THIS Report, which was issued as a confidential document in 1941, is now published as Special Report No. 33. It was included in the programme of papers presented at the Autumn Meeting of The Iron and Steel Institute, held in London, at The Institution of Civil Engineers, on 13th and 14th November, 1946. The work described was the outcome of a co-operative effort carried out by a number of interested firms who agreed to pool their knowledge and carry out joint research on the problem of monolithic dolomite linings for furnaces. Having regard to the fact that most of the magnesite and chrome ore normally used in basic refractories in 1939 consisted of imported materials, it became a matter of national importance when the war broke out to accelerate the search for alternative methods of lining furnaces. The obvious step was to make use of the sources of dolomite available in Great Britain. Representatives of the companies originally interested in this work met and formed the Basic Furnace Linings Committee. This Committee appointed a Technical Panel and by October, 1940, the stage had been reached when large-scale practical trials with dolomite prepared from indigenous materials could be made, and their application in open-hearth furnaces investigated. By the middle of 1941 so much work had been done that it was considered advisable to make the information available to industry. This was done at a confidential meeting at York on 12th September, 1941. The Report was also discussed at Leeds, at a session of the Open-Hearth Conference, on 6th November, 1941. As the need for secrecy no longer exists, the Report has been reprinted and is now published together with discussion and correspondence.

SYNOPSIS.

The Report is divided into six main sections and opens with a Summary by M. Douglas and R. J. Sarjant.

Section I., by A. L. Bradley, J. H. Chesters, and M. Douglas, deals with the properties of dolomite and the manufacture and testing of "basic." An authoritative study of the fundamental character of dolomite is outlined, together with a description of the essential features of the preparation of run-of-kiln "basic" which is supplied commercially for furnace purposes. In the dis-

cussion of the physical properties and chemical composition of this material, special attention has been devoted to the question of hydration tendency in its bearing on the practical use of the commercial basic. Recommended methods of testing are detailed. An Addendum to this Section, contributed by A. L. Bradley and A. H. Jay, records a study of the atomic structure of dolomite and the structural changes produced during heating.

In Section II. A. H. B. Cross, D. F. Marshall, and R. J. Sarjant deal with the pertinent facts relating to the preparation of "basic" in the form

suitable for furnace linings. The preparation of basic comprises two distinct stages of production : (a) A crushing from run-of-kiln size in a primary crusher or perforated-bottom pan mill to a size under $\frac{3}{4}$ in., and (b) grinding in a pan mill, at which stage tar may be added.

A. H. B. Cross and T. R. Walker have recorded, in Section III., the course of experiments with electric-arc-furnace linings. The paper describes the standard practice of lining prior to the development of the new technique at the English Steel Corporation, Ltd., The United Steel Companies, Ltd., and Messrs. Hadfields, Ltd., and records in detail the various stages of development through which this work progressed. Some reference is made to the problem of fettling, but it is indicated that this is a subject on which further research is being undertaken. Examples are given of the most modern technique adopted in the lining of the largest furnaces, and a note is added on the composition and structure of the graded hearth material after it has been in use for some time.

Section IV., a paper by J. C. Hayman, D. F. Marshall, and E. Shaw, describes a technique which has been evolved to produce a more durable bottom for the basic open-hearth furnace. A fundamental principle is the reduction of the intergranular porosity of the rammed material by grinding in solid-bottom pan mills for a specified time. The preparation of the material and the technique of ramming are discussed in

detail, and the methods of bringing the rammed hearths into operation are compared. A summary is given of the practical methods of hearth installation at various plants.

Section V., by A. L. Bradley, J. H. Chesters, J. M. Ferguson, and R. J. Sarjant, is devoted to the basic open-hearth furnace. This paper is noteworthy for the new information contained in it regarding the composition of the hearth and the reactions with the furnace charge which govern its durability. Data are provided to show the serviceability of dolomite bricks as a substitute for magnesite bricks in the sub-hearth. An Addendum comprises a description of the technique of construction and composition at various depths of a monolithic dolomite brick wall, together with a useful note on the reaction between "basic" and other refractory materials likely to be brought in contact with it in the furnace.

Section VI. is contributed by W. Bell, and deals with the preparation and utilization of dolomite at the Corby works of Messrs. Stewarts and Lloyds, Ltd. A detailed description of the dolomite plant is given, including plant layout and notes on the crushers and mills used in the preparation of the tarred-dolomite mixture intended for lining both the converters and the electric furnace. The influence of various factors, notably the silicon content of the iron used, on the life of dolomite linings is discussed in the terms of the detailed investigation carried out on converter bottoms.

FIRST REPORT OF THE ROLLING-MILL RESEARCH SUB-COMMITTEE OF THE IRON AND STEEL INDUSTRIAL RESEARCH COUNCIL.

THIS Report, published as Special Report No. 34, was included in the programme of papers presented at the Autumn Meeting of The Iron and Steel Institute, held in London, at The Institution of Civil Engineers, on 13th and 14th November, 1946.

The Rolling-Mill Research Sub-Committee of the Iron and Steel Industrial Research Council was formed in 1930 and was first concerned with factors determining the efficiency of rolling-mill operation. In 1936 and 1937 a series of conferences was called to examine the possibilities of research into the problems of plant design; these were attended by British rolling-mill plant designers and managers, and scientists interested in allied problems. A panel was appointed to inspect the experimental rolling mills available in Great Britain. This Panel reported that there was no experimental mill then available which would offer suitable facilities, but, pending the provisions of such a mill, it was recommended that : (a) The examination of the published literature on this subject, which had already been started, should be continued, (b) a survey should be made of the existing unpublished technical knowledge of rolling-mill operation, (c) a report should be submitted on the instruments available for rolling-mill research, and (d) investigations should be made at selected mills where certain facilities might be obtained for working on ferrous and non-ferrous materials. The Rolling-

Mill Research Sub-Committee was formed to direct this work, and a full account of the progress made in carrying out the recommendations is presented in this Special Report, of which a synopsis is given below :

SYNOPSIS.

The Report is divided into five Sections. In the introduction (Section I.), E. C. Evans describes the steps, a summary of which is given above, which led to the formation of the Rolling-Mill Research Sub-Committee, and briefly explains the contents of the Report.

The Panel's recommendation that the published literature should be surveyed has been carried out by L. R. Underwood who presents, in Section II., a critical survey of the literature on rolling-mill research. This review concludes with a summary setting out certain very definite primary problems in rolling-mill research which require further elucidation and proposals for a scheme of research involving : (1) Quantitative verification of von Karman's or other friction-hill theory of the pressure distribution between the roll and the material; (2) experimental determination of the natural resistance to flow, free from friction effects, for hot and cold rolling; (3) the investigation of the effects of front and back tension in cold rolling; (4) the investigation of the magnitude and effect of roll flattening; (5) subsidiary problems. The classified bibliography at the end of this section contains 184 references.

Section III., by H. Ford, contains a detailed

description of the experimental rolling mill at the Metallurgical Department of the University of Sheffield and the equipment fitted to it to enable the work in view to be carried out; this included Ward-Leonard control, regulating gear, coilers, and tensioning equipment. The special instruments for making the required measurements are also described. The experimental programme is well under way.

In Section III. mention is made of the instrument which was developed for the measurement of roll-separating force. In Section IV., A. L. M. Douglas and H. Ford deal fully with the measurement of this force. They discuss the methods which have been used in the past and the reasons why the new method was developed. The circuits used in the new unit are described and full details are presented of the pressure head, together with details of calibration tests.

In Section V., E. Orowan and K. J. Pascoe discuss methods of calculating the distribution of roll pressure over the arc of contact in hot flat rolling. For everyday computations in rolling-mill practice speed of calculation is often more important than high accuracy, so that approximate methods of computation are desirable. A simple approximate method of roll-load and torque calculation for hot flat rolling is explained in this Section.

SECOND REPORT ON THE DEVELOPMENT OF MONOLITHIC DOLOMITE LININGS.

By THE TECHNICAL PANEL OF THE BASIC FURNACE LININGS COMMITTEE.

THIS Report was included in the programme of papers presented at the Autumn Meeting of The Iron and Steel Institute, held in London, at The Institution of Civil Engineers, on 13th and 14th November, 1946. It is published as Special Report No. 35, and contains papers on the properties of doloma, in particular, the bulk density, angle of repose, chemical analysis, and thermal conductivity, with additional sections on the fettling of open-hearth and electric furnaces, basic Bessemer converters, and mixer ladles.

SYNOPSIS.

The Report is divided into five sections, and contains also a general survey of the Report, by M. Douglas and R. J. Sarjant.

Section I., a paper by A. L. Bradley, J. H. Chesters, and D. F. Marshall, on the properties of fettling materials, may be regarded as forming a detailed statement of the properties of doloma in relation to its uses for monolithic furnace

linings. A considerable amount of research carried out since the publication of the First Report is described, and close study will reveal a number of fruitful directions in which further investigation might well be continued. In the first Addendum to Section I., W. L. Kerlie describes a comprehensive experimental investigation on the tar bonding of doloma. This had for its purpose the study of the optimum tar content and firing temperature of tarred doloma,

considered from the standpoint of cold crushing strength and durability in storage. An analysis of the operation of twelve pan mills forms the second Addendum, by D. F. Marshall. It is an extension of the comparative study described in the First Report (Special Report No. 33).

Section II., by J. H. Chesters, F. L. Robertson, and E. Shaw, deals with the fettling of open-hearth furnaces and contains a considerable amount of data obtained from shop practice, including the results of a questionnaire addressed to British steelmaking shops. Five Addenda are included in Section II., on "Miscellaneous Factors Affecting Hearth Life," by the authors of Section II., "Monolithic Doloma Doors and Wing Walls," by R. C. Baker, "Tap-Hole Construction and Maintenance," by E. Shaw, "An Analysis of Factors Affecting the Consumption of Doloma in Open-Hearth Furnaces," by A. Brown and D. H. Ward, and "The Development of a Simple Repair Technique for Holes in Doloma Hearths," by E. Shaw.

In Section III., W. L. Kerlie, R. J. Sarjant, and T. R. Walker describe the technique employed in the preparation, ramming, and putting into service of both dry and tarred doloma for the hearths of electric-arc furnaces. Grading of fettling material, methods of application, and factors affecting fettling consumption and bottom life are discussed. A standard lining technique applicable to the installation of monolithic doloma side walls is outlined, together with the results of chemical, mineralogical, and X-ray

examination of the changes in the monolith during service.

"The Applications of Doloma in Basic Bessemer Converters" is the subject of Section IV., by W. D. Kerlie. The effects of stabilized dolomite, hard-burned doloma, and additions of scale, bauxite, and coke to the normal soft-fired doloma have been investigated, and the influence of varying percentages of doloma recovered from old linings on the performance of converter bottoms has been considered. Notes are included on the effect of milling time, manganese and silicon contents of the iron, iron temperature, conditions of firing the lining of the converter, and the tar content of the tarred doloma.

Section V., also by W. L. Kerlie, on the utilization of doloma in mixer ladles, consists of a description of the relining methods adopted and of the results obtained during service on three 25-ton mixer ladles, of which one was lined with stabilized dolomite brick and the other two with tarred doloma, rammed behind a retaining wall of (a) firebrick and (b) stabilized dolomite brick. The experience showed that rammed doloma in mixing ladles stands up much better to the chemical and temperature conditions than firebrick or stabilized doloma bricks, but does not withstand the mechanical effect of the metal stream. A suggestion is made that in mixer and open-hearth-furnace construction the introduction of rammed doloma side walls behind a retaining wall of stabilized doloma brickwork is a question worth pursuing.

SYMPOSIUM ON THE HARDENABILITY OF STEEL.

ORGANIZED BY THE TECHNICAL ADVISORY COMMITTEE OF THE SPECIAL AND ALLOY STEELS COMMITTEE (MINISTRY OF SUPPLY) AND THE IRON AND STEEL INSTITUTE.

This Symposium, which was included in the programme of papers presented at the Autumn Meeting of The Iron and Steel Institute, held in London, at the Institution of Civil Engineers, on 13th and 14th November, 1946, is published as Special Report No. 36. It gives an account of the work done by the Hardenability Sub-Committee of the Technical Advisory Committee which was set up on the return of a small mission of British metallurgists from their discussions in the United States and Canada on means of conserving critical alloys used in steel production. This Sub-Committee had three principal tasks, namely: (a) To standardize the Jominy end-quench hardenability test; (b) to examine the fundamental principles governing the test and to recommend the best methods of interpreting the results; and (c) to survey a representative set of British Standard En steels by hardenability tests and to correlate the results with mechanical properties.

SYNOPSIS.

The Symposium contains twenty-four papers. The first, Section IA, is a Preface by the late Dr. T. Swinden. Section IB gives the constitution of the Hardenability Sub-Committee (as at 1st June,

1945) and in Section IC, D. A. Oliver introduces the Symposium.

Section II. is in two parts, dealing respectively with the effect on Jominy hardenability curves of changes in test conditions and with the reproducibility of these curves. Both parts

are joint contributions from the firms taking part in the research.

Section III. gives full details of the standard procedure for carrying out the Jominy end-quench test.

Section IV. contains three papers. In the first, by T. F. Russell, the theoretical aspects of the end-quench tests are considered; the second, by T. F. Russell and J. C. Williamson, reports an investigation of the surface temperature in the cooling of a Jominy test-piece; and in the third paper, by W. I. Pumphrey and F. W. Jones, Jominy test results are correlated with data from quenched cylindrical bars.

H. Allsop, in Section VA, discusses the significance of variation in Jominy hardenability with respect to mechanical properties. Variations in composition of the order of those permitted by specifications are considered by W. E. Bardgett in Section VB. Sections VC and VD deal respectively with the variation in end-quench hardenability (a) between a number of casts of each of several En specifications, and (b) between different samples from the same cast. These two papers are contributed by the firms concerned with the investigations. In the fifth paper of Section V., E. H. Bucknall presents a note on the effect of the location of the test-piece on the hardenability of billets.

Section VI., devoted to investigations on the relationship between the Jominy hardenability

and the mechanical properties of several steels representing the different types in the En series, contains the following papers: "Hardenability and Mechanical Properties of a Series of B.S. En Steels," by the firms concerned with the investigation; "A Study of the Relationship between End-Quench Hardenability Curves and the Hardness of Bars Quenched in Oil," by H. Allsop and W. Steven; "Observations on the Relationship between Hardenability and the Mechanical Properties of Quenched and Tempered Steels," by W. E. Cooper and N. P. Allen; and "Hardenability Tests of Low-Alloy British Standard Engineering Steels," by W. Crafts and J. L. Lamont.

Studies of (a) the effect of the major alloying elements and of boron on hardenability, by J. Glen, and (b) the hardenability of a hyper-eutectoid chromium-molybdenum steel, by W. I. Pumphrey and F. W. Jones, are reported in Sections VIIA and VIIB respectively.

A summarized statement of the information to be derived from the end-quench hardenability curve, together with the principal conclusions resulting from the Sub-Committee's work, are given in Section VIII, and an account of the Sub-Committee's activities and some suggestions for future research are set forth in Section IX. Finally, Section X consists of a bibliography of 255 references covering the literature from 1938 to 1944.

THE INFLUENCE OF PORT DESIGN ON OPEN-HEARTH FURNACE FLAMES.

By J. H. CHESTERS, D.Sc.(TECH.) (The United Steel Companies, Ltd., Stocksbridge, near Sheffield) and M. W. THRING, M.A., F.INST.P. (The British Coal Utilisation Research Association, London).

This Report, published as Special Report No. 37, was included in the programme of papers presented at the Autumn Meeting of The Iron and Steel Institute, held in London, at The Institution of Civil Engineers, on 13th and 14th November, 1946. It was discussed jointly with a paper on "A Heat-Flow Meter for Use in Furnaces," by R. H. Baulk and M. W. Thring (*Journal of The Iron and Steel Institute*, 1946, No. I., p. 41 P); the discussion is recorded under the title "Discussion on the Influence of Port Design on Open-Hearth Furnace Flames," on pp. 433 P-464 P of this volume.

A Synopsis of the Report is given below, and abstracts of the subject-matter will be found on pp. 89 A-94 A of the present volume.

SYNOPSIS.

Lack of fundamental information on the combustion process in the laboratory of the open-hearth furnace makes it impossible to design a furnace in the sense that a bridge is designed.

The purpose of the trials described in this Report was to obtain some of this information by studying the effect of different port designs on the combustion, heat transfer, and gas flow. This in turn was to be correlated with output rates. It was with this object in view that in 1945 The

United Steel Companies, Ltd., formed an Open-Hearth Advisory Committee. Important work has been done by The British Coal Utilization Research Association, and the Advisory Committee asked for, and obtained, the very valuable assistance of the Association in solving some of the problems which arose. The trials were carried out at the Templeborough shops of Messrs. Steel, Peech and Tozer, on furnaces of different design, namely, an old design, a streamlined design, and a Mearz design. The trial casts were controlled as closely as possible, to allow comparisons to be made. External factors, such as the gas and air pressure, CO_2 in waste gases, and metallurgical load, were carefully measured, and heat-flow

meters, a narrow-angle radiometer, roof pyrometers, &c., were used to study the internal radiation. Preheat and waste-gas temperatures were recorded, using suction pyrometers, and the factors affecting preheat were analysed. The flame location, velocity, and stability, and the rate of mixing of the gases, were studied by means of slow-motion cinematograph films and by a multiple sampling probe inserted through the roof.

A full account of the trials made with this equipment is presented in the Report, which is divided into three main sections entitled "Design of the Experiments" (3 parts), "The Experiments" (14 parts), and "Interpretation of the Results" (2 parts).

OBITUARY

Sir FRANCIS SAMUELSON died at his home at Thirsk, Yorkshire, on January 3, 1946, at the age of eighty-four. After being educated at Rugby, and Balliol College, Oxford, where he graduated in 1885, he succeeded his father, Sir Bernard Samuelson, one of the pioneers of the Cleveland iron trade and President of The Iron and Steel Institute from 1884 to 1885, as Chairman of Sir B. Samuelson and Co., Ltd., of Middlesbrough. The properties of the company were later acquired by Messrs. Dorman, Long and Co., Ltd., Sir Francis being appointed a Director of that concern. For several years he was Chairman of the Tees Conservancy Commission.

He was elected a Member of The Iron and Steel Institute in 1885 and served for twelve years on the Council (Member 1910–1917, Vice-President 1917–1922) before becoming President for the years 1922–1924. He took a prominent part in the organization of the Institute Meeting in Italy in 1923.

Professor LÉON GUILLET died suddenly on May 9, 1946, at the age of seventy-two. He received a Secondary School education in his native town, Saint Nazaire, before going in 1894 to the École Centrale des Arts et Manufactures, where he took the degrees of Ingénieur des Arts et Manufactures in 1897 and Doctor of Physical Science in 1902. On leaving the École Centrale he was given charge of the testing laboratories of the Établissements de Dion, which under his direction soon became a centre of research. In 1906 he was appointed to the Chair of Metallurgy at the Conservatoire des Arts et Métiers and in 1913 to be Professor of General and Non-Ferrous Metallurgy at the École Centrale, of which he subsequently became President. He was elected President of the Société des Ingénieurs Civils de France in 1923 and to the Académie des Sciences in 1925.

Professor Guillet's main scientific work was done in the sphere of physical metallurgy. His studies on structural classifications and equilibrium diagrams for special steels are very well known. He published papers on the influence of third elements in the copper-zinc and copper-tin systems, cementation, nitriding, the hardening of steels and non-ferrous alloys, and tempering, often in association with M. Portevin. The Iron and Steel Institute published the following of his papers :

"Use of Vanadium in Metallurgy" (*Journal*, 1905, No. II.).

"Steel Used for Motor Car Construction in France" (*Journal*, 1905, No. II.).

"Quaternary Steels" (*Journal*, 1906, No. II.).

"Boron Steels" (*Journal*, 1907, No. II.).

"Electrolytic Iron, its Manufacture, Properties, and Uses" (*Journal*, 1914, No. II.).

"The Position of the Metallurgical Industries of Northern and Eastern France : their Destruction and Reconstruction" (*Journal*, 1914, No. II.).

Throughout his career, in his writing, his teaching, and the organization of conferences and centres of study and research, he endeavoured to apply the results of research to industry.

He was elected a Member of The Iron and Steel Institute in 1905, and an Honorary Vice-President in 1937.

Professor ALEXANDER BAIKOFF died in Russia during April, 1946. A pupil of Mendeleieff and Le Chatelier, he introduced into Russian metallurgy the methods of exact research and experiment. When appointed to the position of Professor at the Polytechnic, in Leningrad, he organized a school for the training of metallurgists which became famous throughout Russia, and he carried out research on rails and concrete at the Railway Institute. Among his published works are a textbook on "General Metallurgy," his papers to the First Congress of Russian Metallurgists in 1924, and his "Dialectics of Metallurgical Processes," written in 1932.

After the October Revolution in 1917, Professor Baikoff's public activities increased. He became a member of the Supreme Council of National Economy, Chairman of the Rails Committee of the Ministry of Railways, and consultant to the State Institute of Factory Planning and the Soviet Institute of Metals. In 1932 he was elected to the Academy of Sciences of the U.S.S.R., and in 1937 to be a deputy of the Supreme Soviet. During the recent war he devoted much of his energy to the defence of Leningrad, and his services to the State were recognized by the award of the Order of Lenin on three occasions, and the title of Hero of Socialist Labour.

Professor Baikoff was elected a Member of The Iron and Steel Institute in 1933.

GASTON BARBANSON died on May 4, 1946, at the age of sixty-nine. He was born in Brussels, the descendant of a long line of iron-masters. After completing his studies as a Doctor of Law, M. Barbanson became in 1905 the Manager of the Société Anonyme des Hauts-Fourneaux et Forges de Dudelange. He played a prominent part in the formation of Arbed, joining the Board in 1911 and being elected President in 1919. His in-

fluence in the steel trade spread from Luxemburg throughout Western Europe, and even to South America; in 1926 he was President of the Entente Internationale de l'Acier. On the cessation of hostilities in 1945, he took up his duties in Luxemburg again, and presided at a meeting of Arbed only a week before his death.

M. Barbanson was elected a Member of The Iron and Steel Institute in 1921.

ARTHUR WILLIAM BREARLEY died at Sheffield on November 3, 1946, at the age of seventy-seven. He was engaged in the steel trade for sixty-four years, having started work in 1882 in the crucible department of Messrs. Thos. Firth and Son, Ltd. For some years from 1905 onwards he was employed in Russia at Firth's Salamander Works at Riga. In 1915, with his younger brother, Harry Brearley, the discoverer of stainless steel, he joined Messrs. Brown, Bayley's Steel Works, Ltd. The two brothers were joint authors of a paper read before The Iron and Steel Institute on "Some Properties of Ingots" (*Journal*, 1916, No. II.).

He became a Member of The Iron and Steel Institute in 1908.

CHARLES GEORGE CARLISLE died on January 18, 1946, at the age of sixty-seven. A Mappin Medallist at Sheffield University, he began his career as a metallurgist with Messrs. Thos. Firth and John Brown, Ltd.; in 1920 he founded the firm of Messrs. Carlisle, Wiles & Co., Ltd. (later Messrs. C. G. Carlisle & Co., Ltd.), makers of stainless and high-speed steels and electric-steel castings.

Mr. Carlisle was elected a Member of The Iron and Steel Institute in 1905. In the earlier days he was a frequent contributor to discussions during meetings of the Institute.

HENRI CLAUDE COQUEUGNOT died suddenly on January 22, 1944, at the age of sixty-three. He was educated at the École des Mines and the École Polytechnique, in Paris, and then entered the steel industry. After serving as a lieutenant in the Engineers during the 1914-1918 War, M. Coqueugnot came under the influence of Emile Mayrisch, Gaston Barbanson, and Aloyse Meyer, and joined with them in the expansion of the Luxemburg iron and steel trade between the wars. He became Directeur-Général of the Société Métallurgique des Terres-Rouges and Administrateur-Délégué of the Société Minière des Terres-Rouges, until the formation of Arbed, of which he was appointed a Director. Among numerous other positions connected with the mining and metallurgical industries he held the post of Directeur-Général in Paris of the Usines de Hagondange, until the occupation by the Germans in 1940.

M. Coqueugnot became a Member of The Iron and Steel Institute in 1915.

EDWARD COCKBURN GREIG died at his home in Millhouses, Sheffield, on May 13, 1946. After being educated in Glasgow, he was appointed by the late Mr. James Henderson to the Frodingham Iron and Steel Co., Ltd., where he became in turn chief chemist, rolling-mill manager, and steel-works manager. He took a great interest in labour problems, as a result of which in 1922 he joined the firm of Messrs. Steel, Peech and Tozer as labour manager. Three years later he became works manager, and in 1929 he was appointed Chief Labour Superintendent of The United Steel Companies, Ltd., a position that he retained until his retirement at the age of sixty-eight in March 1946. Mr. Greig was actively interested in the Iron and Steel Trades Employers' Federation, and of the Wages Committee of which he was Chairman for some years.

He was elected a Member of The Iron and Steel Institute in 1917.

EDWIN GILBERT IZOD died on October 2, 1946, at the age of seventy. Born in Portsmouth, he received a general education at Vickery's School, Southsea, before entering an engineering pupilage with Messrs. Maudslay, Sons, and Field, of Lambeth, in whose shops he worked for two and a half years. In 1898 he went to University College, London, as a demonstrator in engineering. Later as Captain H. R. Sankey's assistant at Messrs. Willan and Robinson's, Rugby, he did pioneer work in the development of the application of the theory of entropy to turbine design. It was while he was at Rugby that he discovered, almost by chance during tests on a burst shot-gun barrel, the significance of impact on the physical strength of metals. He did little himself to develop a technique of impact testing with the machine he designed, beyond mentioning his discovery to a few friends. In 1910 he went to Johannesburg as chief consulting mechanical and electrical engineer to the Central Mining Corporation. He retired in 1927 after nine years as Managing Director of Rand Mines, but later accepted the post of Managing Director of Weymann Motor Bodies, Ltd., with whom he worked very strenuously during the war years.

Mr. Izod was elected a Member of The Iron and Steel Institute in 1937.

DAVID LLEWELLYN LLOYD died on December 17, 1945, at the age of sixty-four. He began his business career in 1900 as an apprentice engineer in the foundries, machine shop, and erecting shop of Messrs. Thos. Piggott & Co., Ltd. After being assistant to the general manager and then secretary, he was promoted in 1907 to be general manager. In 1911 he went to the Whitecross Co., Ltd., at Warrington, as technical and commercial assistant to the late Mr. Carson. Early in 1915 he was appointed general manager and a director, and

subsequently Managing Director. Among the official posts which he filled were those of member of the Executive Committee of the Iron and Steel Wire Manufacturers' Association and Vice-President of Warrington Chamber of Commerce.

Mr. Lloyd became a Member of The Iron and Steel Institute in 1913.

THOMAS MORRISON died on October 26, 1946, at Spring Lake, New Jersey, U.S.A., at the age of eighty-five. A native of Scotland, he served an apprenticeship as an engineer and machinist before going to the United States in 1886. His cousin, Andrew Carnegie, appointed him Manager of the Duquesne Works of the Carnegie Steel Corporation in 1891 and General Superintendent of the Edgar Thompson Works four years later. From 1902 until 1911, and from 1914 until 1937 he was a Director of the United States Steel Corporation, and for twenty-nine years a Director of the International Nickel Company. Together with Mr. Julian Kennedy he was responsible for the development of the Kennedy-Morrison process for the slow cooling of rails.

Mr. Morrison was elected a Member of The Iron and Steel Institute in 1895.

TOM SWIFT PEACOCK died at his home at Kingswinford on February 16, 1946, at the age of seventy-seven. He gave up his original intention of studying law to join the iron and steel business of Messrs. John Stansfield and Son. When twenty-three, he became secretary of Messrs. F. W. Cotterill, Ltd., of Darlaston, and later, in 1912, rose to be Managing Director of the firm. After the amalgamation with Messrs. Guest Keen and Nettlefolds, Ltd., he was made Deputy Chairman of the Company. He was also a director of numerous other concerns both in Britain and on the Continent.

Mr. Peacock was elected a Member of The Iron and Steel Institute in 1901.

STANLEY VAUGHAN WILLIAMS died suddenly at his home in Kenton on August 8, 1946, aged forty-three. Born at Brymbo, North Wales, he was educated at Grove Park School, Wrexham, and at University College, Swansea, where he studied metallurgy under Principal C. A. Edwards, F.R.S., and took an honours degree in August, 1924. In October of the same year he began work at the Research Laboratories of the General Electric Co., Ltd., Wembley, and six months later was appointed to the permanent staff. In 1929 he became a member of the leading scientific staff, and in 1938 took over the leadership of the Metallurgical Group.

Mr. Williams joined the Institute of Metals in 1922. He always took an active interest in the London Local Section of that body, and was its

Honorary Secretary from 1936 to 1938, and had been appointed its Chairman for the period 1946-1948. He was one of the first elected (April, 1946) to Fellowship of the newly formed Institution of Metallurgists, a member of the Development Committee of the British Non-Ferrous Metals Research Association, and, since 1945, a Director of Tonfanau Granite Quarries, Ltd. He wrote many papers on metallurgical subjects, and frequently contributed to the technical press.

Mr. Williams became a Member of The Iron and Steel Institute in 1937.

ROBERT WILSON died suddenly in London on February 18, 1946, in his forty-third year. A native of Larkhill, Lanarkshire, and the son of a colliery owner, his family roots were in the coal industry. He decided, however, to adopt metallurgy as a career, and went from school to the Royal Technical College, Glasgow. After serving on the staff of Messrs. Colvilles, Ltd., he joined the Clyde Alloy Steel Co., Ltd., where he remained for several years.

Mr. Wilson joined the editorial staff of the *Iron and Coal Trades Review* in 1928, became their first metallurgical editor, and then assistant editor. He succeeded to the editorial chair early in 1944. Never of very robust health, he suffered a serious illness in the spring of 1945 from which he did not fully recover, although he insisted on remaining in harness. He was very well known throughout the mining and iron and steel industries, in both of which he had a host of friends.

He was a member of a number of technical institutes, including the Institute of Welding and the Institute of Fuel.

Mr. Wilson became a Member of The Iron and Steel Institute in 1928.

HAROLD EDWARD WRIGHT died on March 28, 1946, at his home in Linthorpe, Middlesbrough, at the age of seventy-seven. His career began in 1883 with his appointment as a chief assistant chemist to the North Eastern Steel Works. Later he became blast-furnace and coke-oven manager to Sir Bernhard Samuelson and Co., and metallurgist to the Dorman Long Group after the amalgamation. In 1902, he suggested the use of surplus coke-oven gas for town purposes, and after considerable research and investigation, Middlesbrough became the first local authority to adopt his scheme. He was responsible, too, for the introduction into local blast-furnace practice of the use of rich foreign ores in the Cleveland burden. The high-tensile structural steel "Chromador" was developed in the Dorman Long Research Department under Mr. Wright's direction. He was also concerned in the solution of a wide variety

of technical problems relating to coke, iron and steel manufacture, and corrosion. He presented a paper before The Iron and Steel Institute on "The Chemical and Thermal Conditions in Blast Furnace Practice" (*Journal*, 1920, No. I.).

He was a Past-President of the Cleveland Institution of Engineers and of the Cleveland Scientific and Technical Institution. A triennial lecture before the latter Institution was endowed by Messrs. Dorman, Long and Co., Ltd., as "a token of esteem and gratitude for a lifetime of faithful service." Dr. C. H. Desch, F.R.S., delivered the first "Harold Wright Lecture" in December, 1945. In the same year, The Iron and Steel Institute awarded Mr. Wright the Bessemer Gold Medal, in recognition of his "valuable contributions made over many years to improve the technique of iron and steel manufacture."

He was elected a Member of The Iron and Steel Institute in 1902, and was an Honorary Member of Council during his presidency of the Cleveland Institution of Engineers.

HAROLD BENJAMIN JACKS died in Birmingham on November 27, 1946, at the age of sixty-seven. He began his business career in 1891, when he was thirteen, by joining the firm of Messrs. Darby Brown & Co., of which he became a partner in 1913. For his services in the Ministry of Munitions during the 1914-18 War he was awarded the O.B.E. In 1919 he became provincial sales manager of the Port Talbot Steel Co., Ltd., continuing in this position after the re-organization

with Messrs. Guest Keen Baldwins Iron and Steel Co., Ltd., until his decease.

Mr. Jacks' activities extended to many branches of the iron and steel industry. He was a Founder and Past-President of the Birmingham Metallurgical Society, a member of the Committee of the Birmingham Exchange, and a Past-President of the Staffordshire Iron and Steel Institute. He was also a prominent Freemason.

He became a Member of The Iron and Steel Institute in 1925.

THOMAS HOSKINSON died in December, 1946. Born at Ipswich in 1882, he began his career as assistant manager of the furnaces of the West Yorkshire Iron and Coal Co. Later he became assistant blast-furnace manager at the Park Gate Iron and Steel Co., Ltd., and from 1914 to 1920 blast-furnace manager at the Corby works of Lloyd's Ironstone Company. The last twenty-six years of his life were spent as blast-furnace manager of the Round Oak Steel Works, Limited, Brierley Hill, Staffs. Mr. Hoskinson took an active interest in both the technical and commercial aspects of the iron industry. He was elected President of the South Staffordshire Iron and Steel Institute in 1930, and held the position of honorary treasurer of that body from 1938 until his death. He was also a prominent member of the Joint Iron Council under the presidency of Mr. Harold Berresford.

Mr. Hoskinson became a Member of The Iron and Steel Institute in 1921.

SECTION II.

A SURVEY OF LITERATURE ON THE MANUFACTURE AND PROPERTIES OF IRON AND STEEL, AND KINDRED SUBJECTS.

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Abstractors and Translators : Mr. R. A. RONNEBECK and Dr. D. R. STEINER.

ORES—MINING AND TREATMENT

Ore Preparation. P. F. Grove. (Iron and Steel, 1946, vol. 23, Apr., pp. 139-141). An electrical control, indication, and communication system for the operation of a large ore-crushing, bedding, screening and distribution plant is described.

Late Developments in the Beneficiation of Lake Superior Iron Ores. G. J. Holt. (Blast Furnace and Steel Plant, 1946, vol. 34, Jan., pp. 77-84). Improvements to iron-ore beneficiation plant on the Mesabi plant are outlined with special reference to a new machine combining the action of centrifugal force and rising hydraulic currents.

System for Preparing Ore at the Minnequa Works of the Colorado Fuel and Iron Corporation. R. R. Williams, jun. (Blast Furnace and Steel Plant, 1946, vol. 34, Jan., pp. 108-114). Descriptions are given of the Robins-Messiter ore-reclaiming machine and the crushing, screening, and Dwight-Lloyd sintering plants at the works of the Colorado Fuel and Iron Corporation.

Concentration of Oxide Manganese Ores from Callam County, Wash. (Madeline, Lakeview, and Victory Claims). T. F. Mitchell and W. J. Long.

(United States Bureau of Mines, Dec., 1945, Report of Investigations No. 3837). This Report is one of a series giving results of laboratory and pilot-plant investigations of western manganese ores begun in 1940. The samples tested represented an extremely intimate and complex association of manganese oxide minerals with silica and iron. No effective concentration by ore-dressing methods was possible, and leaching processes are to be tried.

Beneficiation of Iron Ore Draws Continued Attention. E. W. Davis. (Engineering and Mining Journal, 1946, vol. 147, Feb., pp. 108-110). The activities of the leading steelmakers in the United States in the field of iron-ore concentration are briefly reviewed, with special reference to the treatment of low-grade ores and the treatment of tailings.

New Reagents and Methods Mark Ore-Dressing Advance. S. A. Falconer. (Engineering and Mining Journal, 1946, vol. 147, Feb., pp. 104-107, 167-170). Progress made during 1945 in methods of concentrating ores are reviewed. A description is given of a 10-ton/hr. flotation plant operating on Mesabi iron ores.

FUEL

Mining and Utilization of German Brown Coal in the Cologne Area. (British Intelligence Objectives Sub-Committee, Final Report No. 162, 1946: H.M. Stationery Office). Data are given on the occurrence and characteristics of Rheinisch brown coal, and on the organization and production of the industry. Information is provided on the briquetting of brown coal without a binder, together with a report on visits to five power-stations with boilers fired with brown coal, two of these being modern high-pressure stations operating at 100 atm.

Steam Generation in Steel Mills. F. X. Gilg. (Blast Furnace and Steel Plant, 1946, vol. 34, Jan., pp. 138-144). A review of some modern American boiler installations for generating electricity is presented. Four-drum Stirling boilers and two-drum integral-furnace boilers with completely water-cooled furnaces and multi-fuel burners are now generally accepted as being ideal for steelworks service.

Steinkohlen-Bergwerk Rheinpreussen, Moers-Meerbeck (Homberg). (Combined Intelligence Objectives Sub-Committee, File No. XXV-6, 1945: H.M. Stationery Office). Descriptions are given of the equipment and processes at the colliery undertaking of Steinkohlen-Bergwerk Rheinpreussen A.G., Moers-Meerbeck, at the time of the occupation by the American Army in March, 1945.

Kaiser Wilhelm Institut für Kohlenforschung, Mülheim. (Combined Intelligence Objectives Sub-Committee, File No. XXV-1, 1945: H.M. Stationery Office). Information on the work being done at the above Institute, obtained in the course of a visit in April, 1945, is reported.

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Fuel Research and Technology, Bergbau Verein, Essen-Heisingen. (Combined Intelligence Objectives Sub-Committee, File No. XXXI-25, 1945: H.M. Stationery Office). A report on the activities and organization of the Verein für die bergbaulichen Interessen and the Gesellschaft für Kohlentechnik is presented.

Fuel Technology and the Reichsvereinigung Kohle, Essen-Bredeney. (Combined Intelligence Objectives Sub-Committee, File No. XXXI-28, 1945: H.M. Stationery Office). An account is given of the organization and activities of the Reichsvereinigung Kohle.

Wirtschaftliche Forschungsgesellschaft m.b.H. (WIFO) Fuel Blending Station, Heiligenstadt, Germany. (Combined Intelligence Objectives Sub-Committee, File No. XXVII-93, 1945: H.M. Stationery Office). A description is given of one of the smaller German Army Command depôts used for blending, testing, and packaging fuels and lubricants for the German army.

Coal and Coke Research at H. Koppers G.m.b.H., Essen. (Combined Intelligence Objectives Sub-Committee, File No. XXXI-31, 1945: H.M. Stationery Office). Information is given on work done at the laboratories of H. Koppers G.m.b.H., Essen. Investigations have been made on a laboratory scale as well as on a large scale on the gasification of pulverized coal with steam and oxygen.

Fuel Research Activities of the A.G. Kohlenwertstoff-Verbände, Bochum. (Combined Intelligence Objectives Sub-Committee, File No. XXXI-29, 1945: H.M. Stationery Office). Information is given on the

properties, production, and distribution of the by-products of the carbonization of coal in Germany. The above Association is made up of seven important companies controlling the sale of the by-products.

The Preparation of Ultra-Clean Coal at the Königin Elizabeth Colliery, Essen-Frillendorf (Mannesmann-röhren Werke A.G.). (Combined Intelligence Objectives Sub-Committee, File No. XXXIII-6, 1945: H.M. Stationery Office). A short account is given of the coal-cleaning processes employed at the above colliery, where about 12,000 tons of coal are prepared per annum, some of it being used for manufacturing carbon electrodes.

The Control of Deliveries and Methods of Analysing Charcoal. H. Bergström and H. Jansson. (Jernkontorets Annaler, 1946, vol. 130, No. 3, pp. 89-117). (In Swedish). A comprehensive account is given of methods for: (1) Measuring the volume of truck-loads of charcoal; (2) taking samples from trucks and from sacks; (3) determining its friability; and (4) determining the moisture, loss on ignition, carbon and tar contents, capacity for taking up oxygen and giving off carbon dioxide, ignition temperature, ash, and phosphorus content.

Lurgi Gesellschaft für Wärmetechnik, Lurgi House, Frankfurt-am-Main. (Combined Intelligence Objectives Sub-Committee, File No. XXXII-91, 1945: H.M. Stationery Office). This report deals with the activities of the Lurgi Company in the fields of low-temperature carbonization, active carbon, distillation of light hydrocarbons, high-pressure gasification, and Fischer-Tropsch synthesis. It also contains information on the cost of producing oxygen.

H. Koppers G.m.b.H., Essen. (Combined Intelligence Objectives Sub-Committee, File No. XXVIII-36, 1945: H.M. Stationery Office). Information obtained as a result of a visit in April, 1945, to H. Koppers G.m.b.H., when the Company's activities relating to the low-temperature carbonization of coal and the gasification of coal to make synthesis gas were investigated, is reported.

Disposal of Sludge from Acid Washing of Coke-Oven Light Oil. (Eastern States Blast Furnace and Coke Oven Association and Blast Furnace and Coke Association of the Chicago District: Blast Furnace and Steel Plant, 1946, vol. 34, Jan., pp. 121-125, 127). The literature on methods of disposing of acid sludges from coke-oven plants and oil-refining plants is reviewed. There are two principal types of process. In one, steam is used to separate the acid from the hydrocarbons, and the volatile products are drawn off and can be distilled and refined. In the other, the sludge is burnt and the sulphur dioxide formed is reconverted to sulphuric acid; a special burner with steam ports arranged tangentially at the end of the nozzle has been designed for this purpose, the object being to atomize the sludge away from the burner tip. It is suggested that some of the oil-refinery processes could be applied to coke-oven by-product sludge.

Coal-Extraction Plant of Ruhröl G.m.b.H. at the Hugo Stinnes Werke of the Mathias Stinnes Gewerkschaft at Welheim near Bottrop i.W. (Combined Intelligence Objectives Sub-Committee, File No.

XXXI-27, 1945: H.M. Stationery Office). A report is presented giving information obtained during a visit in June, 1945, to the coal-extraction plant at Welheim in Westphalia, which is associated with a hydrogenation plant. One of the major advances in the technical operation of the process during the war was a new filtering system using specially developed ceramic filters of high porosity that permitted recovery of an extract containing only 0.05% of ash.

Thyssen'sche Gas und Wasserwerke G.m.b.H., Duisberg-Hamborn, and Krupp Treibstoffwerk, Wanne-Eickel, Thyssen-Galocsy Gas Producer. (Combined Intelligence Objectives Sub-Committee, File No. XXIX-51, 1945: H.M. Stationery Office). A short account is given of the Thyssen-Galocsy slagging gas-producer process and plant at Hamborn and Wanne-Eickel. In this process oxygen and steam, instead of air, are blown into the entrance chamber of the producer, in which there is ignited any combustible matter in such quantity that the resulting gas mixture is heated up to the temperature at which steam and carbon dioxide are able to react quickly with hot carbon. In the second stage of the process this hot mixture is admitted to the solid fuel in the shaft of the producer, together with sufficient excess oxygen for the heat attained by the combustion of carbon to carbon monoxide to cover the heat required for the decomposition of the steam and carbon dioxide, and, if desired, the reduction of ore.

Fischer-Tropsch Unit at Leipzig Gas Works. (Combined Intelligence Objectives Sub-Committee, File No. XXVII-68, 1945: H.M. Stationery Office). A short description is given of the Fischer-Tropsch plant and process at the gas works at Leipzig. This plant was installed for the purpose of enriching the town gas and at the same time increasing the recovery of liquid and solid hydrocarbon products. The description applies to its condition in April, 1945.

Fischer-Tropsch and Allied Processes. (Combined Intelligence Objectives Sub-Committee, File No. XXVII-82, 1945: H.M. Stationery Office). A description is given of the development of the Fischer-Tropsch and allied processes in Germany, the information being based on interviews with H. Pichler and H. Koch of the Kaiser Wilhelm Institut für Kohlenforschung at Mülheim.

The Fischer-Tropsch Plant of Ruhrchemie A.G., Sterkrade-Holten, Ruhr. (Combined Intelligence Objectives Sub-Committee, File No. XXVII-69, 1945: H.M. Stationery Office). An account is given of the plant and processes at the works of Ruhrchemie A.G., at Sterkrade. This Company owned the exclusive rights of the Fischer-Tropsch process, and this works served as the research and development centre for the process. The plant was inspected in April, 1945, and the description of the processes is based on interrogations of some of the staff of the works.

Plant of Klocknerwerke A.G., Castrop-Rauxel. (Combined Intelligence Objectives Sub-Committee, File No. XXV-7, 1945: H.M. Stationery Office). An account is given of an inspection of the plant and processes at the Castrop-Rauxel works of Klocknerwerke A.G., which took place in April, 1945. This plant is in two distinct sections: (1) A colliery with

coke-ovens and by-product plant, and (2) a synthetic-ammonia plant and Fischer-Tropsch plant.

The Offices of Gutehoffnungshütte A.G. (G.H.H.) Sterkrade, Ruhr. (Combined Intelligence Objectives Sub-Committee, File No. XXVII-70, 1945: H.M. Stationery Office). This Report contains information obtained at the above works on the design of the reaction vessels used in Fischer-Tropsch process.

Inspection of Hydrogenation and Fischer-Tropsch Plants in Western Germany during September, 1945. (British Intelligence Objectives Sub-Committee, Final Report No. 82, 1945: H.M. Stationery Office).

Developments at four hydrogenation plants and six Fischer-Tropsch plants in Western Germany from May to September, 1945, and plans for their reconstruction and future operations are reviewed.

Botrop-Welheim Hydrogenation Plant. (Combined Intelligence Objectives Sub-Committee, File No. XXX-104, 1945: H.M. Stationery Office). These notes combine the results of interrogating plant personnel with information extracted from documents at the works, and they give a general picture of the operations carried out at the Welheim hydrogenation plant during the war.

PRODUCTION OF IRON

Improvements in Blast Furnaces in the Past Quarter Century. L. E. Riddle. (Blast Furnace and Steel Plant, 1946, vol. 34, Jan., pp. 87-92). Improvements in blast-furnace design, hot-blast stoves, blast mains, cleaning equipment for blast-furnace gas, charging equipment, iron and slag transport equipment, tuyeres, instruments, and blast-conditioning plant are briefly reviewed.

Part I. I.G. Farben Industrie-Oppau Works, Ludwigshafen (Report on Nickel and Iron Powder Plants). **Part II. Nord Deutsche Affinerie, Hamburg (Report on the Treatment of Nickel-Copper Ores and Residues).** (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 263: H.M. Stationery Office). The production of nickel and iron powders at the Oppau works of I.G. Farbenindustrie is described.

Ferro-Alloy Production at the Badische Wolframerg G.m.b.H., Solingen bei Karlsruhe. (Combined Intelligence Objectives Sub-Committee, File No. XXX-55, 1946: H.M. Stationery Office). A brief account is given of the above plant, at which there now remain four out of the seven electric furnaces which produced ferrochromium, ferrotungsten and ferromolybdenum.

Elektrowerk-Weisweiler at Weisweiler near Eschweiler. (Combined Intelligence Objectives Sub-Committee, File No. XI-13, 1945: H.M. Stationery Office). An inspection of this works, at which ferroalloys containing silicon, manganese, chromium, molybdenum, and tungsten were made, was carried out in November, 1944, and the present report covers the plant lay-out, the equipment still there, a list of that removed, the electrical characteristics of the furnaces, and data regarding the number of furnaces operating between May, 1943, and September, 1944.

Manufacture of Ferrous Metal Powder Parts. P. Schwarzkopf and C. G. Goetzel. (Metal Progress, 1946, vol. 49, Mar., pp. 539-547). The manufacture of parts of intricate shape from iron powder by powder metallurgy is described in detail with many illustrations of the machinery and processes involved.

Carbursintering of Iron Powders. A. S. Margolies. (Iron Age, 1946, vol. 157, Feb. 28, pp. 60-63). A description is given of a powder-metallurgy procedure in which iron powder is compacted at 25, 50, and 75 tons/sq.in., and then carburized and sintered simultaneously for various periods at 1700° F. in a container with the carburizing compound. Increasing the compacting pressure and decreasing the carburizing time resulted in improved physical and mechanical properties and deeper cases. Increasing the compacting pressure also raised the carbon content of the cases and lowered that of the core.

Resistivity Measurements on Iron and Steel Compacts. R. Steinitz. (Powder Metallurgy Bulletin, 1946, vol. 1, Jan., pp. 6-7). Experiments are described in which the electrical resistivity of compacts of iron powders, mixtures of iron and graphite, and two alloy steel powder mixtures were measured after pressing at 25 and 50 tons/sq.in., and after pressing at 50 tons/sq.in. and sintering for 15 min. at 700° and 1090° C. A short sintering period rapidly reduces the resistivity of an unsintered compact which indicates that an actual metallic bond between particles starts in the first stages of sintering.

Cemented Steels. E. S. Kopecki. (Iron Age, 1946, vol. 157, May 2, pp. 50-54). A powder-metallurgy technique is described which consists of heating a porous part made of iron or steel powder in contact with a copper alloy to a temperature above the melting point of the alloy; the molten alloy then fills up all the voids in the compact and, on cooling, all the particles are welded together. Materials with tensile strengths between 60,000 and 100,000 lb./sq.in. have been obtained by this process. Cheap raw materials and low compacting pressures render the process economical. Parts made in this way can be readily brazed without a flux and the surfaces obtained are sufficiently smooth and dense to permit electroplating without infiltration of the plating solution.

FOUNDRY PRACTICE

German Steel Foundry Methods. (Combined Intelligence Objectives Sub-Committee, File No. XXVI-86, 1945 : H.M. Stationery Office). A report on methods employed at German steel foundries, based on visits to the Bochumer Verein, Krupp, Skodawerke, Ruhrstahl, and Reickserke plants, is presented.

Report on German Steel Foundries. (British Intelligence Objectives Sub-Committee, Final Report No. 109, 1945 : H.M. Stationery Office). A survey of German steel foundries with particular regard to layout, equipment, and production practice is presented.

Robert Bosch, Stuttgart and Feuerbach. (Combined Intelligence Objectives Sub-Committee, File No. XXVII-91, 1945 : H.M. Stationery Office). A report is presented on the foundries, heat-treatment shops, and finishing departments at the Stuttgart and Feuerbach works of Robert Bosch A.G. and the work that was done there during the war.

Slags and Fluxes. H. Lepp. (Metal Industry, 1946, vol. 68, Mar. 15, pp. 203-205; Mar. 22, pp. 227-228; Mar. 29, pp. 252-253; Apr. 5, pp. 266-268). The use of slags and fluxes in metallurgy throughout the ages is briefly reviewed in Part I. In Part II. the terms "slag," "flux," and "dross" are defined and the application of slags in the foundry is discussed. The reactions involved in desulphurizing iron and copper are considered in Parts III. and IV.

Increases Malleable Iron Capacity. P. Dwyer. (Foundry, 1946, vol. 74, Mar., pp. 90-94). An illustrated description is given of the reconstruction which was carried out at the works of the Albion Malleable Iron Co., Albion, Michigan, in order to bring the production up to about 150 tons of iron per day.

The Foundry Helps Out. (Iron and Steel, 1946, vol. 23, Apr., pp. 149-150). A description is given of the design for a cast steel rear spar for an aeroplane which replaced a fabricated component comprising 69 tubes and forgings.

German Cast Armour. (Combined Intelligence Objectives Sub-Committee, File No. XXVII-78, 1945 : H.M. Stationery Office). Specifications for German cast steel armour for tanks and combat vehicles are considered with information on its heat-treatment and repair by welding.

Ruhrstahl A.G., Annener Works, Witten-Annen. (Combined Intelligence Objectives Sub-Committee, File No. XXIX-26, 1945 : H.M. Stationery Office). A report on the plant, equipment, and processes at the above works, where steel castings of high quality and forged die blocks were made, is presented.

High Quality Steel Castings. Ruhrstahl A.G., Annen. (Combined Intelligence Objectives Sub-Committee, File No. XXXI-42, 1946 : H.M. Stationery Office). A description is given of the electric-furnace steel plant and processes at the works of Ruhrstahl A.G., Annen, where about 3200 tons of steel for castings and 800 tons for forging were produced per month.

Stahlwerk Krieger Oberkassel. (Combined Intelligence Objectives Sub-Committee, File No. XXVII-100, 1945 : H.M. Stationery Office). A brief description is given of the plant and products of the above works. The principal products were cast steel ship's propellers, conning-towers, stern frames for submarines, cast armour for tanks, turbine casings, and manganese steel castings.

Methods of Testing Prepared Foundry Sands. (Institute of British Foundrymen, 1945, Nov.). This is the First Report of the Joint Committee on Sand Testing, the Joint Committee consisting of representatives of The British Cast Iron Research Association, The British Non-Ferrous Metals Research Association, The Institute of British Foundrymen, and The Iron and Steel Institute. The Report describes methods and recommended procedures for the routine testing of all types of prepared moulding and core sand.

Preventing Gray Iron Surface Roughness. E. V. Somers. (Foundry, 1946, vol. 74, Mar., pp. 84-87, 171). An investigation is reported in which the effects of ferrostatic pressure, section size, mould ramming, baking and blacking practice, and pouring temperature on the surface quality of grey cast iron were studied. The test castings were made in series of five cylinders all 5 in. in dia. with heights of $\frac{1}{2}$, $\frac{3}{4}$, 1, 2, and 3 in. respectively. Any mechanical method of reducing the porosity of the mould surface, such as harder ramming or coating with blacking, reduces the penetration of metal into the mould surface and decreases the amount of trapped sand. Lowering the pouring temperature increases the surface tension and decreases the fluidity, and therefore tends to decrease the penetration of the metal into the mould. When making castings with a high ferrostatic pressure in the drag and a low pressure in the cope it is practicable to spray blacking in the drag only.

Core Blowing Practice. L. D. Pridmore. (American Foundrymen's Association : Foundry, 1946, vol. 74, Mar., pp. 95, 168-171). Some different types of core-blowing machines are described and practical questions on core-blower operation are answered.

Fried. Krupp A.G., Grusonwerke, Magdeburg. (Combined Intelligence Objectives Sub-Committee, File No. XXVIII-64, 1946 : H.M. Stationery Office). A short account of the melting and casting technique in the manufacture of chilled rolls at the above works is given.

German Facilities for the Production of Centrifugally Cast Gun Tubes. (Combined Intelligence Objectives Sub-Committee, File No. XXIX-39, 1945 : H.M. Stationery Office). A report is presented on the facilities in Germany for the centrifugal casting of gun barrels. In particular, descriptions are given of the "Deutsche Eisenwerke" and "Buderus" centrifugal casting machines.

Deutsche Edelstahlwerke A.G., Hochfrequenz-Tiegelstahl G.m.b.H., Bochum. (Combined Intelligence Objectives Sub-Committee, File No. XXVII-

40, 1945 : H.M. Stationery Office). A description is given of the machine and process for the centrifugal casting of tubes of austenitic steel. The water-cooled inclined mould could be revolved at up to 2000 r.p.m. and the machine could make tubes from 140 to 450 mm. in outside dia. The water-cooled mould was coated with a layer of sand 4 mm. thick, which gave it a long life. A combination of centrifugal casting with subsequent pilger rolling was very successful for the production of long, thin-walled tubes.

Bochumer Verein A.G., Abt. Stahlwerke Bochum. (Combined Intelligence Objectives Sub-Committee, File No. XXVII-42, 1945 : H.M. Stationery Office).

The centrifugal casting of steel gun barrels at the plant of the Bochumer Verein is described.

Special Alloy Steel Manufacture and Centrifugal Casting of Alloy Tubes and Gun Barrels. (Combined Intelligence Objectives Sub-Committee, File No. XXXI-46, 1946 : H.M. Stationery Office). A description is given of the steel-making unit, foundry, and heat-treatment and machine shops at the works of Hochfrequenz-Tiegelstahl G.m.b.H., Bochum.

Acceptance Standards. (Automobile Engineer, 1946, vol. 36, Mar., pp. 101-104). The determination of casting quality by radiography and X-ray micrography is discussed, and a method of establishing standards for the acceptance of castings is described.

PRODUCTION OF STEEL

Klockner Werke A.G., Hagen-Haspe. (Combined Intelligence Objectives Sub-Committee, File No. XXIX-61, 1945 : H.M. Stationery Office). A report on the war-time activities of the iron and steel works and collieries of Klockner Werke A.G. is presented.

Hermann Göring Steel Works, Paul Fleige Hütte, Stahlwerke, Braunschweig. (Combined Intelligence Objectives Sub-Committee, File No. XXIX-30, 1945 : H. M. Stationery Office). This report covers investigations of the conditions at the ore mines, blast-furnaces, steel furnaces, rolling mills, foundry and forging plants, and shell-machining shops of the Hermann Göring Corporation in the vicinity of Watenstedt-Salzgitter.

Röchling'sche Eisen und Stahlwerke G.m.b.H. (Combined Intelligence Objectives Sub-Committee, File No. XXII-3, 1945 : H.M. Stationery Office). A brief report on the expansion of production and the technical developments which have taken place at the Völklingen Works of Röchling'sche Eisen und Stahlwerke G.m.b.H. is presented. The developments include the desulphurization of liquid pig-iron with liquid soda ash, the recovery of vanadium from pig-iron by a unique process, the improvement of coke-oven gas by the Still process, and the construction of the all-basic open-hearth furnace. The problem of the all-basic open-hearth furnace has apparently been solved in Germany during the war. The three furnaces constructed with basic roofs at this works have apparently been giving very satisfactory operation. Both magnesite and chromium-magnesite bricks were used, and, in spite of the heavy duty imposed on the furnace in the manufacture of high-class steels, a furnace life of up to 1400 heats between repairs was achieved.

Friedrich-Alfred-Hütte at Rheinhausen, Germany. (Combined Intelligence Objectives Sub-Committee, File No. XXIV-10, 1945 : H.M. Stationery Office). Descriptions are given of the plant and processes at the Rheinhausen Works of the Krupp concern. This was a high-production plant for normal commercial products; no alloy steel of any kind was made. It is probable that the data reported are representative of approximately three-quarters of the whole German steel industry.

Gebrüder Bohler A.G. at Buderich, Germany. (Combined Intelligence Objectives Sub-Committee, File No. XXV-14, 1945 : H.M. Stationery Office). The plant and processes at the Buderich works of Gebrüder Bohler A.G. in the condition in which they were found in April, 1945, are described. Alloy steels and tool steels were made there, and one department produced cemented carbides by the powder-metallurgy process.

Investigation of Rheinmetall-Borsig A.G., Düsseldorf. (Combined Intelligence Objectives Sub-Committee, File No. XXVII-79, 1945 : H.M. Stationery Office). An account is given of the organization of Rheinmetall-Borsig A.G., and of the work done during the war at the Düsseldorf plant of this Company.

The Rheinmetall-Borsig Works and Proving Grounds at Unterluss. (Combined Intelligence Objectives Sub-Committee, File No. XXVII-65, 1945 : H.M. Stationery Office).

Burbach Eisenhütte, Saarbrücken. (Combined Intelligence Objectives Sub-Committee, File No. XX-6, 1945 : H.M. Stationery Office). An inspection of the iron and steel works of Burbach Eisenhütte near Saarbrücken was made in March, 1945, a short account of which is given in this report, which contains a brief description of the plant and its past and present productive capacity.

The Deutsche Edelstahlwerke, Krefeld, Germany. (Combined Intelligence Objectives Sub-Committee, File No. XXIV-28, 1945 : H.M. Stationery Office). A description is given of the plant and processes at the works of the Deutsche Edelstahlwerke A.G., Krefeld, as inspected in March, 1945. This works had an ingot capacity of 10,500 tons of electric-furnace steel and 4500 tons of open-hearth steel per month.

Deutsche Edelstahlwerke, Krefeld, Germany. (Combined Intelligence Objectives Sub-Committee, File No. XXV-38, 1945 : H.M. Stationery Office). A second inspection of this plant was made in April, 1945, and this report contains a more detailed description of the rolling mills, cold-finishing shop, forge shop, and powder-metallurgy department.

Deutsche Edelstahlwerke Aktiengesellschaft, Kre-

field, Germany. (Combined Intelligence Objectives Sub-Committee, File No. XXVII-62, 1945: H.M. Stationery Office). A description is given of the laboratories and production equipment at the works of the Deutsche Edelstahlwerke A.G., and of their activities during the war.

August Thyssen Hütte A.G., Hamborn. (Combined Intelligence Objectives Sub-Committee, File No. XXVI-32, 1945: H.M. Stationery Office). An account is given of the war-time activities at the works of August Thyssen Hütte A.G., Hamborn. A process for recovering vanadium was developed. Fine Gällivara ore, low in gangue, was added to the basic-Bessemer iron in the mixers; the resulting slag was skimmed off and collected and the dust from the converter hoods was also collected. This slag and dust were sent to Ruhrort-Meiderich for smelting and reoxidation by blowing or trommelling, and the vanadium was subsequently recovered from the slag by chemical extraction. Attempts were made to improve the quality of the basic-Bessemer steel by preventing the absorption of nitrogen. The time required for blowing was reduced by using oxygen-enriched air and by adding calcium carbonate, mill-scale, or iron ore to the charge, and by washing the iron in the mixers. To prevent too high a temperature being reached, cold steel scrap was added after 70-80% of the blow. Ferro-alloys were added after the blow to obtain sufficient temperature for proper pouring.

Open-Hearth Steel Making Practice at Gusstahl-Fabrikation. (Combined Intelligence Objectives Sub-Committee, File No. XXXI-48, 1946: H.M. Stationery Office). An account is given of the steel-making practice at the above works in Germany.

Steel Making in Belgium and Luxembourg during German Occupation. (Combined Intelligence Objectives Sub-Committee, File No. XII-21, 1945: H.M. Stationery Office). As a result of a visit to the Belgian Iron and Steel Federation in Brussels and to the Belval Works of ARBED, information on steel-making in Belgium and Luxembourg during the war was obtained, and is included in the present report. The only technical developments of importance were the manufacture of H.P.N. steel (a low-phosphorus low-nitrogen steel) and the recovery of vanadium from pig-iron. Notes on the changes in the specification of shell steel and on the measures taken to conserve supplies of manganese are included.

Alloy and Tool Steel Manufacture in India. P. H. Kutar. (Thirty-third Indian Science Congress: Metallurgia, 1946, vol. 33, Mar., pp. 261-264). **Alloy and Tool Steel.** P. H. Kutar. (Iron and Steel, 1946, vol. 23, Apr., pp. 151-157). An account is given of developments in India in the manufacture of alloy steels and tool steels during the war years 1940-45. The manufacture of the high-tensile steel "Tiscrom" and the low-alloy weldable steel "Tiscor" was greatly increased. In order to replace cold hematite pig-iron in steelmaking, an all-scrap-charge process was introduced; in this, petroleum coke was added to the charge to provide the carbon. Permanent-magnet steels, high-silicon steel sheets for

transformers, tool steel, and corrosion- and heat-resistings were all successfully manufactured.

Crucible Steel. (Iron and Steel, 1946, vol. 19, Apr., pp. 135-138). An historical account of crucible steelmaking at Grenoside and Masbro' near Sheffield is given, with notes on the personalities concerned.

Symposium on Deoxidation. (American Institute of Mining and Metallurgical Engineers, 1945, vol. 162, pp. 656-736). A symposium on deoxidation in steel-making was held at Cleveland, Ohio, on October 18, 1944, at which the following papers were presented:

Deoxidation of Basic Open-Hearth Steel, by T. S. Washburn.

Slag-Metal-Oxygen Relationships in the Basic Open-Hearth and Electric Processes, by J. S. Marsh.

The Total Oxygen Content of Plain Carbon Open-Hearth Steel during Deoxidation and Teeming, by M. Tenenbaum and C. C. Brown.

The Occurrence of Oxygen in Liquid Open-Hearth Steel—Sampling Methods, by T. E. Brower and B. M. Larsen.

Effect of Deoxidation on the Strain-Sensitivity of Low-Carbon Steels, by H. K. Work and D. Enzian.

The Relation among Aluminium, Sulphur, and Grain Size, by C. E. Sims.

Operating an 180-Ton Open Hearth Furnace with Ends and Roof of Basic Construction. A. K. Moore. (Blast Furnace and Steel Plant, 1946, vol. 34, Jan., pp. 97-99). Experience gained in the operation of a 180-ton open-hearth furnace with ends and roof of basic brick at the works of the Steel Co. of Canada, Ltd., is reported. Relative data for all-basic and all-silica linings, respectively, are: (1) Steel produced from charging to tapping 17.14 and 15.75 tons/hr.; (2) average times per heat 10 hr. 45 min. and 11 hr. 40 min.; (3) lost time per heat 53 min. and 36 min.; and (4) fuel oil consumptions 26.3 and 24.3 U.S. gallons per ton of steel. The all-basic furnace was taken off for general repairs with a roof life of 331 heats and 832 heats to the credit of the ends.

The Use of Mexican Graphite Lowers Open Hearth Melting Costs. R. J. Zemanek. (Blast Furnace and Steel Plant, 1946, vol. 34, Jan., pp. 100-104). Recommendations on basic and acid open-hearth practice are made for cases where Mexican graphite is charged to supply the carbon when the proportion of pig-iron used is low. Operating data for both cold- and hot-metal charges are presented and the costs of production are compared.

Some Quality Considerations in Current Open Hearth Production. H. J. Forsyth. (Blast Furnace and Steel Plant, 1946, vol. 34, Jan., pp. 93-96). Improvements and the trend of development in open-hearth practice as reported in recent literature are reviewed.

The "Elkem" Rotating Arc Furnace for Electrothermic Process. T. Ellefsen. (Electrochemical Society, Apr., 1946, Preprint No. 12). The difficulties caused by crater formation under the electrodes in electric arc furnaces are pointed out and a description

is given of the recently developed Norwegian "Elkem" rotating arc furnace. In this design the three electrodes move in the vertical plane only whilst the body of the furnace, which is mounted on a turntable, is slowly rotated (the speed can be adjusted between 6 hr. and 96 hr. per revolution). The furnace has three tapholes and one movable tapping bridge which follows the rotating movement. A comparison is made of the costs of making 75% ferrosilicon in this furnace and in a stationary one. The former produced 17% more than the latter with the same power consumption. This furnace has also been described by Bo Kalling and A. Lindblad (*see* Journ. I. and S.I., 1943, No. I., p. 42 A).

Switchgear and Control Developments Aid in Successful Operation of the Modern Arc Furnace. W. N. Gittings. (Steel, 1946, vol. 118, Mar. 4, pp. 146-148, 186-194). Descriptions are given of the Magneblast power circuit breaker and the amplidyne generator and their application in the control of electric-arc melting furnaces.

Electrode Regulation for Modern Electric Furnaces. A. G. Arend. (British Steelmaker, 1946, vol. 12, Apr., pp. 184-187). The precision regulation and hydraulic-electric control of the movement of electrodes in modern carbon-arc melting furnaces are described, and details are given of the Söderberg system of making the electrodes above the furnace itself, in which the carbon mixture and binding material are passed into a cylinder made of sheet metal and moved down into the furnace.

Coreless Induction Furnaces. M. J. Marchbanks. (Institution of Electrical Engineers, 1946, Preprint). Coreless induction furnaces for steel melting and case-hardening are dealt with. The construction of the furnace bodies to avoid heating of the metal framework and the fritting of refractory linings *in situ* are discussed. Other apparatus in the furnace circuit is described—namely, high-frequency generators, switches for condensers, and the protection of the generator. The changing characteristics of furnaces due to changes in the physical properties of the charge and the effects of lining erosion, and valve-operated furnaces are also considered.

Remote Control. C. G. White. (British Engineer-

ing Export Journal, 1946, vol. 28, Mar., pp. 666-671). Illustrated descriptions with wiring diagrams are given of recent developments in the application of supervisory remote control to electrical networks, including the transmission and distribution of electricity for steelworks.

Steelmaking Alloys. H. Brearley. (British Steelmaker, 1946, vol. 12, Mar., pp. 120-123). The influence of manganese, ferrochromium, and nickel in steelmaking is discussed. A plea is made for simplification in the presentation of the results of tests.

The Origin and Constitution of Certain Non-Metallic Inclusions in Steel. J. R. Rait and H. W. Pinder. (Iron and Steel Institute, 1946, this Journal, Section I). The phase diagrams relating to the study of non-metallic inclusions in steel are reviewed, and the important ternary system $\text{MnO-Al}_2\text{O}_3\text{-SiO}_2$ examined; the most probable phases occurring in the complex system $\text{CaO-MgO-FeO-MnO-SiO}_2\text{-Al}_2\text{O}_3$ are described in the light of the review. A large number of different types of inclusions in acid open-hearth and basic electric-furnace steels (direct-poured, tundish-poured, and bottom-poured) are identified by extraction and by the use of phase-diagram data, chemical analysis, metallographic examination, and X-ray examination.

It has been possible to ascertain the sources of many of these inclusions with a fair degree of accuracy, and a table summarizing these results is given.

Practical suggestions are made for reducing the incidence of harmful non-metallic inclusions in steel.

Production Statistics, German Steel Industry 1943 and 1944. (Combined Intelligence Objectives Sub-Committee, File No. XXVIII-54, 1945: H.M. Stationery Office).

Mill Building Ventilation. D. Henderson. (Steel, 1946, vol. 118, Mar. 11, pp. 98-99, 111, 112). A description is given of the air heating and ventilation system installed in a building 528 ft. long \times 171 ft. wide used for making 8-in. shells. The building contained reheating furnaces, forging machinery, and finishing machines, and can be taken as a typical example of the ventilation difficulties to be overcome in a steelworks.

FORGING, STAMPING, AND DRAWING

Steel Forging Industry of Germany. (Combined Intelligence Objectives Sub-Committee, File No. XXVI-69, 1945: H.M. Stationery Office). This Report is based on observations made during visits to German forging plants in March, April, May, and June, 1945, by teams of metallurgists.

Tovarna Na Nabojky A Kovove Zbozi (Patronen Hülsen und Metallwaren Fabrik) Rokycany, Czechoslovakia. (Combined Intelligence Objectives Sub-Committee, File No. XXVII-41, 1945: H.M. Stationery Office). This works produced finished sheets in brass, bronze, copper, and steel, as well as certain metal fittings for buildings. The plant is briefly

described and the manufacture of brass and steel shell cases is reported on.

German Machinery Spring Industry. (Combined Intelligence Objectives Sub-Committee, File No. XXVIII-15, 1945: H.M. Stationery Office). A report is presented on the equipment at German works where gun springs, clock and watch springs, and valve springs are made.

German Spring Making Industry. (British Intelligence Objectives Sub-Committee, Final Report No. 181, 1945: H.M. Stationery Office). The Report is presented of a mission which examined German technique and developments in the manu-

facture, machinery, materials, and finishes applied in making all types of springs; it also studied the markets served and the working conditions in the industry so far as they affected these markets.

Cold-Die Quenching. A. F. Gollistel. (Steel, 1946, vol. 118, Mar. 4, pp. 129, 172-178). Some examples of the use of water-cooled dies for the simultaneous pressing and hardening of small parts are described and illustrated.

The Effect of Material in Deep Drawing Operations. (Machine Shop Magazine, 1946, vol. 7, Mar., pp.

49-56). The requirements of a material for deep-drawing operations are pointed out and the effects of the average grain size, the grain-size distribution, and preferred orientation are discussed. The characteristics of the material which can and can not be changed by heat-treatment are referred to.

Surface Preparation for Cold Drawing Steels. R. Saxton. (Machinist, 1946, vol. 89, Apr. 6, pp. 2631-2633). The processes of patenting, pickling, liming, and baking in the preparation of wire rod for drawing are described.

ROLLING-MILL PRACTICE

Output of Rolling Mills and Auxiliary Equipment Increased by Electrical Developments. F. Mohler. (Blast Furnace and Steel Plant, 1946, vol. 34, Jan., pp. 118-120). Examples are cited which illustrate the improvements in rolling-mill speeds and mill-motor control which have been achieved in the United States by the application of amplidyne control of generator voltage, of load balance between twin drives, of the tension reel, and of ohm-drop compensation.

Electronics in Engineering. W. Wilson. (Institution of Production Engineers, 1946, vol. 25, Apr., pp. 113-134). Of the developments in electronic apparatus that have taken place during the last ten years, the following examples are selected for special comment: (a) The grid-controlled mercury arc rectifier; (b) the inverter; (c) the ignitron; and (d) the magic eye. The principles of these are explained and it is shown that the criticism that the use of glass valves and flimsy metal components is out of place in engineering works is no longer valid. Many applications of electronic devices are described such as high-frequency heating, resistance welding, motor

control, voltage regulators, synchroscopes, cathode-ray tubes, and the electron microscope.

Computations of Rolling Load, Torque, and Roll-Face Pressure in Metal Strip Rolling. M. Cook and E. C. Larke. (Journal of the Institute of Metals, 1945, vol. 71, Nov., pp. 557-579). The effects of roll diameter, initial thickness, amount of reduction, and the frictional forces encountered between the rolls and the metal, on the magnitude of the rolling load, roll torque, and roll-face pressure in the rolling of copper strip, have been determined by applying the Orowan graphical method of calculation and the formulæ of Ekelund.

The Cold Rolling of Strip Sections for Aircraft. N. S. Aston. (Journal of the Institution of Engineers, 1943, vol. 54, Part I, pp. 1-11). The cold-rolling of complicated sections from strip of steel, aluminium, and light alloys is described. The paper is in four parts as follows, the third being treated at considerable length: (1) Types of section and their uses; (2) various methods of production; (3) the power rolling process; and (4) tool design office procedure.

PYROMETRY

Temperature Measurement by Means of an Immersion Pyrometer. E. Hunter, A. R. Parkes, and J. W. Dews. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 78, Jan. 17, pp. 53-60). A detailed description is given of a platinum/platinum-rhodium immersion pyrometer which was developed at a foundry, the object being to provide an accurate method of controlling at a reasonable cost the temperatures of high steel mixes.

Improvement in Design of Immersion Pyrometers for Liquid Steel Temperatures. D. Manterfield and J. R. Thurston. (Iron and Steel Institute, 1946, this Journal, Section I). An improved design of immersion thermocouple for open-hearth furnaces, consisting of a semi-permanent fixture attached to the back-wall furnace binding, is described. It is manipulated through the back wall of the furnace by means of a light jib. The apparatus is easy to manipulate; it requires only one operator and little maintenance is necessary. A steel end-block which has an extremely

long life and eliminates the troubles caused by embrittlement of the rare-metal couple wires is also described. Suggestions regarding further improvements, including an all-steel arm for the back-wall installation, are made.

Recent Developments in the Pyrometry of Liquid Iron and Steel. H. T. Clark. (Iron and Steel Engineer, 1946, vol. 23, Feb., pp. 55-62). The suitability of the following thermocouples for determining the temperature of liquid iron and steel is discussed: (1) Tungsten-molybdenum; (2) tungsten-graphite; (3) carbon/silicon-carbide; and (4) platinum/platinum-rhodium. Radiation-measuring pyrometers are also described with many references to the literature. The two methods of temperature measurement which the author considers to be most practical are the platinum/platinum-rhodium thermocouple and the open-end-tube immersion pyrometer with a photoelectric cell or a total radiation pickup.

HEAT-TREATMENT

Gas-Carburizing. I. Jenkins. (Iron and Steel Institute, 1946, this Journal, Section I). The mechanism of carburization in solid and in gaseous media is discussed, and it is shown that in pack-carburizing the atmosphere surrounding the work is rich in carbon monoxide and hydrogen. It is considered that the hydrogen plays an active rôle in the basic carburizing reactions, possibly by forming hydrocarbon gases which carburize the steel or by promoting the removal of surface films of carbon dioxide.

The ideal carburizing atmosphere is one which maintains the maximum rate of carburization throughout the period of treatment, is readily controlled to give the desired carbon content and depth of case, and does not stain the work. Raw hydrocarbon gases, such as town gas, propane, &c., give rise to heavy sooting which interferes with the carburization process and leads to poor and non-homogeneous cases. Sooting can be reduced by diluting the hydrocarbon, and results are reported of the carburization of commercial case-hardening steels in propane diluted with air and with burnt town gas. Whereas heavy cases of hypereutectoid composition can be obtained, the presence of active decarburizing agents in the diluting atmosphere necessitates a high concentration of propane in order to obtain the maximum rate of carburization, and such conditions lead to excessive sooting of the work. A more suitable diluting medium is one containing no active decarburizing gases, and in this respect controlled atmospheres which are sensibly free from carbon dioxide and water vapour have given very encouraging results. The concentration of hydrocarbon necessary to give the maximum rate of carburization is sufficiently small to reduce sooting to negligible proportions, and control over the surface concentration of carbon in the case is readily achieved. Controlled atmospheres containing carbon monoxide and hydrogen, with or without nitrogen, and approaching the composition of the atmosphere found in pack-carburizing experiments, have proved to be quite strong carburizing agents; brief details of the generation of such atmospheres and the results obtained in carburizing commercial steels with them are reported.

The condition of the steel surface before carburization may have a marked effect upon the rate of carbon absorption, and it has been found that activation of the surface by "gas-etching" leads to a very pronounced increase in the rate of carburization above that obtained with rolled or machined surfaces.

It is shown that carburization of steel near to its A_3 point can lead to a non-homogeneous case, and the mechanism of carburization below the A_3 point is discussed.

A brief note is added on the relative stabilities of cementite and of solid carbon, following certain observations during the work on gaseous carburizing processes.

Gas Carburising. (Engineer, 1946, vol. 181, Apr. 26, pp. 382-383). A description is given of a gas-

carburizing plant for which it is claimed that any quality or depth of case can be produced in the minimum of time under conditions of great economy and reliability. The preheating and carburizing phases are under strict control and a diffusion period can be provided if desired. The installation consists of several furnace bases and work covers, one mobile furnace capable of being placed on any base, a gas-preparation plant for the diluting media, a supply of hydrocarbon gas, and master control panels.

Modern Heat-Treat Department Essential to the Manufacture of Allison Engines. W. G. Guthrie. (Industrial Heating, 1946, vol. 13, Mar., pp. 404-420). An illustrated description is given of the heat-treatment department at a branch of General Motors Corporation making gears for aeroplane engines. The gears travel successively through degreasing, copper-plating, carburizing, annealing, hardening, degreasing, tempering, shot-blasting, and inspection departments.

Fabricating and Heat Treating Push Rods at Ford Rouge Plant. (Industrial Heating, 1946, vol. 13, Jan., pp. 22-28, 148). An illustrated description is given of the heat-treating plant and practice in the mass production of push rods for automobile engines at one of the Ford Motor Company's plants.

Production Line Heat Treatment of Stainless Bar Stock. J. F. Sullivan. (Metal Progress, 1946, vol. 49, Mar., pp. 523-525). A description is given of the heat-treatment plant for stainless steel bars at the works of the Allegheny Ludlum Steel Corporation. It consists of six oil-fired and six electric furnaces of the car-bottom type and the auxiliary equipment.

A Study of Heating Up of Electric-Resistor Furnaces. V. Paschkis. (Industrial Heating, 1946, vol. 13, Feb., pp. 250-260; Mar., pp. 434-438, 460). The influences of the initial rate of energy input and the wall design upon the heating-up time and power consumption of electric resistor furnaces are discussed. The first part deals with the heating up of an empty furnace and the maintenance of the required temperature after the charge has been put in. In the second part calculations are made respecting the effect of the connected load, thermal conductivity, volumetric specific heat, and furnace-wall thickness on the heating-up time for a furnace.

Induction Hardening of Precision Steel Parts. W. Boyle. (Materials and Methods, 1946, vol. 23, Feb., pp. 425-428). Descriptions are given of special inductor coils designed for the induction hardening of a variety of machined parts without distortion.

High Intensity Induction Heating. W. M. Roberds. (Steel, 1946, vol. 118, Mar. 18, pp. 104-107; 161-165). Different techniques for applying high-frequency current to the heating and quenching of bars are described. Micrographs of the surfaces obtained when heating by (a) moving the bar through a short coil, and (b) using a coil long enough to enclose the whole bar are shown and discussed.

"Seven-in-One" Induction Hookup Hardens Navy Gun-Mount Parts. (Industrial Heating, 1946, vol. 13,

Feb., pp. 240-248). A description is given of an induction-heating plant in which inductor blocks for various applications at seven hardening benches are all supplied from one 125-kW. 9600-cycle motor-generator set.

What Frequency for Induction and Dielectric Heating? R. A. Nielson. (Steel, 1946, vol. 118, Mar. 11, pp. 102-106, 112). Formulae are developed for calculating suitable frequencies for the induction heating of conducting materials and the dielectric heating of insulating materials.

Bright Annealing of Wire in Bell-Type Furnace at Atlas Tack Corporation. (Industrial Heating, 1946, vol. 13, Feb., pp. 278-284). An illustrated description is given of an annealing plant for coils of low-

carbon steel wire. A movable cylindrical furnace heated by gas-fired radiant tubes is lowered over the charge which is prepared on a circular base and covered with a bell into which the protective atmosphere is blown.

Cooling Quenching Oils. (Machine Shop Magazine, 1946, vol. 7, Mar., pp. 86-90). Calculations are made showing the rates of heat extraction required to cool the oil in oil-quenching tanks into which various weights of steel are placed. A cooler is described in which a mixture of air and water is used as the cooling medium; in this cooler the greater part of the heat is extracted from the oil by the evaporation of a relatively small quantity of water which is sprayed downwards over the cooling tubes.

WELDING AND CUTTING

Uniwelding Produces High Joint Efficiency. E. R. Proctor. (Iron Age, 1946, vol. 157, Mar. 7, pp. 46-51). An illustrated description is given of the "Uniweld" process in which the joint is made by heating with a multi-tip oxy-acetylene burner while hydraulic pressure is applied to produce a predetermined amount of upset. To obtain the required degree of flame control it was necessary to install flowmeters in the oxygen and acetylene lines and to adjust the flame by the flow rather than the pressure.

Metallurgical Aspects of High Quality Pressure Welded Joints for Landing Gear. Part II. Tests, Set-Up and Inspection. L. Fine, C. H. Maak, and A. R. Ozanich. (Metal Progress, 1946, vol. 49, Mar., pp. 530-536). The Uniweld process of oxy-acetylene welding has already been described (*see* Journ. I. and S.I., 1946, No. I., p. 77 A). The testing and inspection of Uniweld joints in tubing are discussed.

The Spot Welding of NE 8715, NE 8630 and SAE 4340 in the 0.062-In. Thickness. W. F. Hess, W. D. Doty, and W. J. Childs. (Welding Journal, 1946, vol. 25, Feb., pp. 123-S-128-S). The practice of tempering spot welds by a second application of current in the welding machine after allowing a brief time interval in which the surrounding metal "quenches" the weld is now well established. In this paper tests are reported from which were developed the optimum conditions for welding and tempering when making spot welds in low-alloy nickel-chromium-molybdenum steel sheet metal 0.062 in. thick.

Proportioning of Weld Sizes. C. M. Leavitt. (Welding Journal, 1946, vol. 25, Feb., pp. 121-129). The specifying of welds and the proportioning of the sizes of welds in shipbuilding are discussed.

Efficient Arc Welding by Means of Proper Procedures. W. J. Conley. (Welding Journal, 1946, vol. 25, Feb., pp. 131-141). Diagrams and data are presented illustrating procedures for making fillet and butt welds. The effects of changes in rate of electrode movement, current input, and angle of electrode to the work are explained and the importance of the first of these factors on the appearance, strength, and cost of the weld is particularly emphasized.

A Study of Austenitic Welding for Control of Graphitization in Steel. I. A. Rohrig. (Welding Journal, 1946, vol. 25, Feb., pp. 90-S-99-S). Evidence is presented that the formation of the dangerous "chain" type of graphitization which forms at welds in molybdenum steel pipes in high-temperature service may be inhibited by the use of austenitic chromium-nickel steel welding rods. In the tests reported, carbides migrated from the pipe metal adjacent to the weld and were absorbed by the austenitic weld metal instead of decomposing into graphite in the critical zone at the low-temperature edge of the heat-affected parent metal.

Cast Iron Welding. A. S. Prince. (Welding, 1946, vol. 14, Mar., pp. 134-135). A technique is described by which hard spots can be avoided in the oxy-acetylene welding of cast iron. Preheating to red heat and a slightly reducing flame are required; the cold filler rod should not penetrate into the molten puddle and the inner cone of the flame should not impinge on the puddle. As the rod melts in the flame the skin of the rod forms a pipe through which the weld metal flows down and under the skin of the puddle which is being built up.

Arc Welding Electrode Coatings. H. P. Zade. (Welding, 1946, vol. 14, Mar., pp. 127-131). The importance of the concentricity of coatings on welding electrodes is discussed and the following methods of measuring concentricity are described: (1) By micrometers; (2) by optical means; (3) by X-ray shadowgraphs; (4) methods based on measurement of magnetic flux; (5) by dielectric measurement of the coating thickness; and (6) a bridge method in which the core wire and the coating are used as resistances and capacitors in a universal bridge circuit.

Preliminary Study of the Notched-Bead Slow-Bend Test for Weldability of Steels. C. B. Voldrich, R. W. Bennett, and D. C. Martin. (Welding Journal, 1946, vol. 25, Feb., pp. 77-S-90-S). An investigation of different procedures for carrying out notched-bead slow-bend weldability tests on three steels containing carbon 0.30-0.37%, nickel about 0.10%, copper about 0.22%, with manganese contents of 0.76%, 0.89%, and 1.50% respectively, is reported. Either

a square notch with rounded corners or a U-notch with a full root radius functioned satisfactorily. The properties of the specimens changed considerably with time. Ageing for one week at room tem-

perature or at 212° F. for 16 hr. caused a substantial increase in the angle of bend and a slight increase in the maximum load when testing these steels; the reasons for this were not determined.

MACHINING

Hardening Effects of Machining DTD 49B. S. A. J. Sage. (Machinery, 1946, vol. 68, Mar. 28, p. 399). An example of work-hardening caused by machining is described. This occurred in turning a thread on a small cylindrical component of austenitic nickel-chromium steel to Specification DTD 49B. The thread was cut in three stages and the excessive hardening occurred in the second stage by a severe rubbing action in cutting the rough thread with a single-point tool. The trouble was cured by increasing the clearance, keeping the tool sharp, and lowering the speed slightly.

Recent Research in Metal Machining. D. F. Galloway. (Proceedings of the Institution of Mechanical Engineers, 1945, vol. 153, War Emergency Issue No. 4, pp. 113-127). The results of recent research in metal machining are reviewed. Analytical tests to determine the exact nature of the cutting process and the distribution of stresses are first examined, after which the action of cutting fluids and the results of practical research in rough- and finish-turning and in boring are discussed.

Hardening by Grinding. A. Holloway. (Machinery, 1946, vol. 68, Mar. 7, pp. 305-306). Two cases are cited in which undesirable hardness and hardening cracks were caused in ground hexagonal steel bars by the heat of the grinding operation. In one case the

steel contained carbon 0.35% and manganese 1.2%; the other involved a 0.35%-carbon 1%-chromium 3.75%-nickel steel.

Some Effects of Work Positioning When Face-Milling Steel. F. W. Lucht. (Transactions of the A.S.M.E., 1946, vol. 68, Feb., pp. 151-160). There has been little study of the effect of the position of the work relative to the milling cutter in the face-milling of steel, and only in limited cases has any consideration been given to the fact that the radial engagement angle between the face of the tooth and the edge of the work where the cutting edge enters should be negative. Milling operations are frequently found where the diameter of the face mill is too small to permit the proper positioning of the work to a setting which gives the longest cutter life. The problem of determining the optimum cutter diameter for a given face-milling job, and the proper positioning of the work in relation to the cutter, led to a series of studies, the results of which are reported in this paper.

Stainless Steels. (Automobile Engineer, 1946, vol. 36, Mar., pp. 124-126). The tools and techniques are described for the forming, cutting-off, drilling, tapping, threading, reaming, milling, and shaving of stainless steels.

PROPERTIES AND TESTS

Internal Stress and the Fracture of Metals. J. Selwyn Caswell. (Ebbw Vale Metallurgical Society: Metallurgia, 1946, vol. 33, Mar., pp. 236-242). Aspects of the relation between internal stress and the fracture of metals are discussed and methods of reducing the risk of failure are suggested. Internal stresses are divided into the three groups (a) those due to thermal changes, (b) those produced by applied loads, and (c) those due to the motion of mass at high speed, and these are discussed with practical examples. Cyclic stressing and factors affecting fatigue resistance are dealt with next. Finally, a large number of examples of defective and improved designs of parts subjected to variable stress are illustrated and explanatory comments are made.

Running Steel in Contact without Lubrication. R. C. Edwards. (Iron Age, 1946, vol. 157, Feb. 28, pp. 56-57). A series of tests is described the purpose of which was to discover the type of steel most suitable for a particular application in which steel ran against steel without lubrication and without scoring while maintaining flat surfaces. A Timken wear-testing machine was used in which a ring of the steel to be tested was rotated at a surface speed of

400 ft./min. with a 12-lb. load; the test was run until the first sign of scoring appeared on the ring surface. In order to run two metals together without lubrication they should produce a very fine oxide powder. The best results were obtained with a nitrided 5%-chromium steel. Steels higher in chromium seized even though an oxide was artificially introduced.

An Interferometer Type of Dilatometer, and Some Typical Results. L. A. Willey and W. L. Fink. (Transactions of the American Institute of Mining and Metallurgical Engineers, 1945, vol. 162, pp. 642-655). A detailed description is given of the dilatometer apparatus and method used at the Aluminium Research Laboratories. It consists of a Zeiss interference-measuring apparatus, a furnace, and an adjusting stand on which the interferometer is assembled and adjusted before it is placed in the furnace.

Dilatometric Studies of the Graphitization of Cast Iron. N. A. Ziegler. (Transactions of the American Institute of Mining and Metallurgical Engineers, 1945, vol. 162, pp. 627-636). The percentage of combined carbon in grey iron used for enamelling is rather high and some of this carbon is likely to graphitize in the

enamelling process when it is heated to 870–930° C. A study was therefore made of the dimensional changes on heating and cooling specimens of this class of iron in which the manganese/sulphur ratios varied between 1.2 and 30.2. The growth of the grey iron was due primarily to the graphitization of some of the combined carbon. The rate of growth was very rapid and most of it occurred in the 650–850° C. range. The growth increased with increasing amounts of sulphur and decreased with increasing amounts of manganese in the iron.

Practical Applications of Hardenability Testing. D. H. Bell. (Australasian Engineer, 1946, Feb. 7, pp. 35–38). Methods of applying end-quench hardenability curves for controlling heat-treatment operations and determining whether a given heat of steel is satisfactory for the purpose intended are described.

Influence of Certain Factors on the Magnetic Properties of Electric Steel Sheets. J. S. Vatchagandhy and G. P. Contractor. (Journal of Scientific and Industrial Research, 1944, vol. 3, Aug.-Sept., Reprint). An investigation was made on the effects of various heat-treatments on the electrical and magnetic properties of five grades of steel containing from 0.65% to 4.25% of silicon. The conclusions reached were: (1) Any treatment which causes "over-annealing" increases the watt losses; (2) the finishing temperature in the rolling of the sheets affects the structure and requires modification of the annealing treatment; (3) the larger the grain size, the lower the watt losses and the greater the permeability, but there is an optimum grain size above which the magnetic properties deteriorate; (4) the optimum structure for lowest losses and highest permeability consists of large "anhedral" grains with slightly undulating boundaries; polyhedral structure does not show the best results; (5) grains as large as the thickness of the sheet are detrimental; (6) a correct final annealing can counterbalance the differences produced by various rolling schedules; (7) the best finishing temperature is 700–750° C.; (8) the best annealing temperature for steels with 0.60% to 3.50% of silicon is 800–850° C.; for transformer steel, annealing at 950–1000° C. shows the lowest watt losses; and (9) the permeability of silicon steel decreases with the silicon content.

Loss Due to Magnetic Hysteresis in Silicon-Steel Sheets. S. Velayos and V. Sanchez-Giron. (Nature, 1946, vol. 157, May 4, pp. 583–584). The magnetic hysteresis loops for three different sheets of silicon steel were determined in an extensive range of values of magnetic flux density B_{\max} , by the ring-ballistic method. From these loops the energy losses in ergs/cu.cm./cycle for different values of B_{\max} , were derived and the curves obtained by plotting these values against the corresponding values of B_{\max} are presented. The applicability of Steinmetz' empirical law to the data is discussed.

Modern Hard Magnetic Materials. K. Hoselitz. (Journal of Scientific Instruments, 1946, vol. 23, Apr., pp. 65–71). The development of permanent magnet alloys is reviewed with data on some typical compositions with their magnetic properties. Design

calculations for magnets to comply with various requirements are presented and explained. Finally, the magnetization and testing of modern materials are described.

A Rapid Cathode-Ray Method for the Determination of Low Magnetic Susceptibility. J. Convey and O. J. Russell. (Journal of Scientific Instruments, 1946, vol. 23, Apr., pp. 71–72). A description is given of a simple A.C. inductance bridge method developed in the Admiralty Laboratory, Sheffield, to determine the magnetic nature of materials of very low magnetic susceptibility.

Magnetic Materials and Beryllium. (British Intelligence Objectives Sub-Committee, Final Report No. 36, 1946: H.M. Stationery Office). A report is presented on the information obtained on visiting the works of Heraeus Vacuumschmelze A.G., Hanau, where special magnetic alloys, beryllium, and beryllium-copper alloys are prepared.

A Velocity-Modified Temperature for the Plastic Flow of Metals. C. W. MacGregor and J. C. Fisher. (Journal of Applied Mechanics, 1946, vol. 13, Mar., pp. A-11–A-16). A theory for the velocity of plastic flow as a function of temperature and stress has been developed by H. Eyring. On this basis the present authors have developed a "velocity-modified" temperature for representing by means of a single variable the combined effects of strain rate and temperature on the stress reaction in a tensile specimen. Available data are analysed, and they indicate that the velocity-modified temperature is equally applicable to the tensile test, whether conducted at slow or rapid rates, as well as to the creep test.

Stresses in Rotating Disks at High Temperatures. A. S. Thompson. (Journal of Applied Mechanics, 1946, vol. 13, Mar., pp. A-45–A-52). A general method has been found by which the problem of stresses in rotating discs with any arbitrary profile can be solved. The method takes into account the effect of plastic flow and variable temperature, including the change with temperature of the modulus of elasticity, the coefficient of expansion, and the permissible stress. Two examples of the method are given.

Heat-Resisting Alloys for Motor-Car Gas Producers. J. Sissener. (Foundry Trade Journal, 1946, vol. 78, Mar. 28, pp. 341–345). An account is given of the development in Norway of a suitable heat-resistant alloy to replace the 25/20 chromium-nickel steel for the grates of charcoal gas producers for automobiles. A 25%-chromium steel with about 0.30% of carbon, 2% of nickel and 0.20% of nitrogen was found to be suitable. In further tests with the object of reducing the chromium content, a steel was produced containing chromium 7%, aluminium 4%, and carbon 0.5%; it was rather brittle but much superior to cast iron for the above purpose.

Precipitation Hardening Stainless Steel. (Steel, 1946, vol. 118, Mar. 4, pp. 136–138). **New Type Stainless Steel Developed in U.S.A.** (British Steel-maker, 1946, vol. 12, Mar., pp. 143–148). Particulars are now released of a new heat-treatable 18/8 stainless steel called "Stainless W" which was made in the United States during the war. In the annealed state

it has a hardness of Rockwell C 22-28 and a tensile strength of 120,000-150,000 lb./sq.in.; by proper heat-treatment these figures can be raised to 39-47 and 195,000-225,000, respectively.

New Age-Hardening Stainless Steel Provides Strength without Cold Working. T. C. Du Mond. (Materials and Methods, 1946, vol. 23, Feb., pp. 432-433). Particulars are given of the new heat-treatable stainless steel called "Stainless W" (see preceding abstract).

Eleventh Progress Report of the Joint Investigation of Failures in Railroad Rails in Service and Their Prevention. (Illinois University, 1945, Engineering Experiment Station, Reprint Series No. 32). The investigation of the causes of fissures in rails has been continued (see Journ. I. and S.I., 1944, No. II., p. 166 A). The present Progress Report comprises the following papers:

Examination of Controlled Cooled and Brunorized Rails which Failed in Service. R. E. Cramer.

Field Tests for Batter of End-Hardened Rails in Service on the Chesapeake and Ohio Railway. R. S. Jensen.

Examination of Carey End-Hardened Rails for Weeping Cracks. R. E. Cramer.

Progress Report on Web Failures of Rail. H. F. Moore and R. S. Jensen.

Third Progress Report of the Shelly Rail Studies at the University of Illinois. R. E. Cramer.

Progress Report on the Effect of the Ratio of Wheel Diameter to Wheel Load on Extent of Rail Damage. (Illinois University, 1945, Engineering Experiment Station, Reprint Series No. 33). Results are reported of tests using flangeless wheels 33 in. and 50 in. in dia. with various loads on short lengths of 131-lb. flat-bottomed rail in a 12-in. stroke rolling-load test machine in which the ratio of load to wheel-diameter on the wear and hardness of the rail was determined.

Visit to M.A.N. Research Laboratory, Heinrich von Buz Strasse, Augsburg. (Combined Intelligence Objectives Sub-Committee, File No. XXXIII-11, 1946: H.M. Stationery Office). A brief account is given of the type of research work carried out and the testing equipment available in the extensive laboratories of the M.A.N. concern, makers of marine Diesel engines.

METALLOGRAPHY AND CONSTITUTION

New Developments in the Study of Surface Chemistry. E. A. Gulbransen. (Metal Progress, 1946, vol. 49, Mar., pp. 553-559). Descriptions are given of the electron microscope, the electron diffraction camera, and the vacuum microbalance, with examples of their application to the study of metal surfaces and surface reactions.

Geiger Counter Used in Powder Metallurgy. E. S. Kopecki. (Iron Age, 1946, vol. 157, Feb. 28, pp. 48-51). A brief description is given of the Geiger counter X-ray spectrometer with which X-ray intensities and diffraction angles can be measured directly without the necessity for intermediate photographic methods. Its application for the rapid determination of the quantity of tungsten carbide when making tools by powder metallurgy is explained.

The Miscibility Gap in the Fe-S-C System at Carbon Saturation in the 1300-2000° C. Temperature Range. A. Norrö and S. Lundquist. (Jernkontorets Annaler, 1946, vol. 130, No. 3, pp. 118-126). (In Swedish).

The mutual solubility in the liquid state of two phases, one rich in iron and the other rich in sulphur and both saturated with carbon, was determined for temperatures in the 1300-2000° C. range. The solubility curves obtained are presented. The temperature of complete miscibility was found to be 1970° C. at 9.5% sulphur.

A High-Speed Dilatometer and the Transformational Behavior of Six Steels in Cooling. A. L. Christenson, E. C. Nelson, and C. E. Jackson. (Transactions of the American Institute of Mining and Metallurgical Engineers, 1945, vol. 162, pp. 606-622). A detailed description is given of a high-speed dilatometer with which the changes in dimensions of specimens can be followed with cooling rates up to 500° C./sec. The results of observations on low-alloy chromium-molybdenum and chromium-nickel-molybdenum steels and other high-tensile steels are presented and discussed.

ANALYSIS

The Chemical Determination of Tantalum and Niobium in Tungsten-Bearing Heat-Resisting Steels. E. W. Harpham. (Metallurgia, 1946, vol. 33, Mar., pp. 245-247). A brief review of recently published methods for the chemical determination of tantalum and niobium is given, and then a method for the routine determination of tantalum and niobium in tungsten-bearing heat-resisting steels is described. The importance of determining the contents of both elements is pointed out.

The Determination of Carbon in Ferrous Materials. J. B. Cotton. (Analyst, 1945, vol. 70, Dec., pp. 466-468). The relative merits of gravimetric and volumetric finishes to the combustion method for the determination of carbon in ferrous materials are discussed. A semi-automatic method, employing a volumetric finish, which makes use of a barium-chloride/sodium-hydroxide absorbent in evacuated bottles is described. A sketch of the apparatus is shown, and typical results are recorded.

Rapid Method of Determining Minute Quantities of Carbon in Metals. J. K. Stanley and T. D. Yensen. (Industrial and Engineering Chemistry, Analytical Edition, 1945, vol. 17, Nov., pp. 699-702). A method, taking about 20 min., for the determination of amounts of carbon below 0.01% in soft magnetic alloys is described.

Combustion Method for Sulphur Determination in White Cast Iron. J. Hedberg and H. A. Schwartz. (American Foundryman, 1946, vol. 9, Jan., pp. 63-64). A method for determining the sulphur in white cast iron is described. As it takes only 12 min. it is suitable for control in malleable iron foundries. It is a modification of the method described by the Blast-Furnace Materials Analysis Sub-Committee (see Journ. I. and S.I., 1944, No. 1, p. 301 p).

Determination of Metallic Iron and Oxygen in Sponge Iron. J. P. Morris. (United States Bureau of Mines, Sept., 1945, Report of Investigations No. 3824). Several methods for determining metallic iron and oxygen in sponge iron were studied using specially prepared samples of known composition. In the presence of only metallic iron and iron oxides in finely ground samples, the mercuric-chloride method gives accurate results for metallic iron. The copper-sulphate method of C. E. Williams and A. E. Anderson gives values for metallic iron which are much too high. Two hydrogen-evolution methods are described which give accurate results for oxygen and total iron but low values for metallic iron; this also applies to samples containing only metallic iron and iron oxides.

A Method for the Determination of Selenium in Steels, with Notes on the Determination of Sulphur. B. S. Evans. (Analyst, 1946, vol. 71, Feb., pp. 68-70).

Symposium on Determination of Hydrogen in Steel. (Transactions of the American Institute of Mining and Metallurgical Engineers, 1945, vol. 162, pp. 353-412). A symposium on methods of determining hydrogen in steel was held in New York on February 22, 1944. After a brief introduction by J. B. Austin the following papers were presented:

Methods of Analyzing for Hydrogen in Iron and Iron Alloys, by T. D. Yensen and R. K. McGeary.

Vacuum-Fusion Analysis of Steel for Hydrogen, by G. Derge, W. Peifer, and B. Alexander.

Determinations of Hydrogen in Iron and Steel by Vacuum Extraction at 800° C., by J. G. Thompson.

Determination of Hydrogen in Steel Sampling and Analysis, by Vacuum Extraction, by R. M. Scafe.

A Modified Vacuum Extraction Apparatus, by W. D. Brown.

Determination of Hydrogen by Vacuum Extraction and Tin Fusion, by J. Naughton.

Determining the Hydrogen Content of Molten Steel by Vacuum Extraction, by C. B. Post and D. G. Schoffstall.

Determination of Hydrogen in Molten Steel by the Gas-Tube Method, by J. G. Mravec.

Preliminary Experiments on the Total Combustion Method for the Analysis of Hydrogen in Steel, by G. A. Moore.

A New Method for the Absorptiometric Determination of Chromium in Low Alloy Steels by Oxidation with Potassium Bromate. M. Z. De Lippa. (Analyst, 1946, vol. 71, Jan., pp. 34-37). A new absorptiometric method for the determination of chromium in low-alloy steels with a reasonable degree of accuracy, and taking only 20 min. for a single sample, is described.

Application of Colorimetry to the Analysis of Corrosion-Resistant Steels. O. I. Milner. (Industrial and Engineering Chemistry, Analytical Edition, 1946, vol. 18, Feb., pp. 94-96). A rapid photometric method for determining copper in corrosion-resisting steels is described. Twelve determinations can be completed in 2 hr. after the samples have been dissolved.

An Introduction to Metallurgical Spectrographic Analysis. D. M. Smith. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 78, Mar. 21, pp. 311-312). A brief explanation of the fundamentals of spectrographic analysis is given.

Spectroscopy Applied to Ferrous and Nonferrous Metals. W. J. Pochlman. (Welding Journal, 1945, vol. 24, Nov., pp. 564-S-572-S). The development and principles of the spectrograph are explained and its usefulness for the non-destructive analysis of metals in the form of castings, forgings, plates, bars, welding rods, and beads of weld metal is discussed.

Applications of the Intermittent A.C. Arc Technique of Spectrographic Analysis. J. A. C. McClelland. (Analyst, 1946, vol. 71, Mar., pp. 129-138). The intermittent A.C. arc technique has been applied to materials in which the elements are not present in the metallic state; it was considered likely to give satisfactory results in the spectrographic analysis of samples of this nature. Two variants are described, one for very small samples of one or two elements in simple conditions, the other for larger amounts of a number of common elements. In general, an accuracy of about $\pm 5-10\%$ of the proportion of the element present is attainable by either method.

Routine Spectrographic Analysis of Cast Iron. J. E. Hurst and R. V. Riley. (Iron and Steel Institute, 1946, this Journal, Section I). A method for the routine spectrographic analysis of cast iron, which has been used for over a year, is described. The spectrographic technique is found to be ideal for the rapid and accurate analysis of a variety of plain and alloy cast irons for all elements except carbon, sulphur, and phosphorus. The method in use, with modifications, is similar to the flat-surface technique recommended by Barker for steel. The importance of suitable layout of the laboratory, representative analytical samples, and rigid standardization of procedure in the attainment of accuracy in routine analysis, is stressed. The single- and multi-spot methods of sparking are compared, and the considerations affecting the choice of excitation, and the influence of air blast at the analysis gap on the duplication of the results, are dealt with. Details

are given of a method of plate calibration based upon the relative intensities of a group of standard lines in the iron spectrum; the method has enabled a complete analysis of all major metals normally present in cast iron to be estimated accurately from one exposure. Standard chemically-analysed samples are used only for the establishment of "working graphs" from which the percentages of alloying elements in routine samples are read.

Rapid Spectrographic Analysis. F. Rohner. (Schweizer Archiv, 1945, vol. 11, Sept., pp. 311-318). A very rapid technique for making spectrographic analyses for purposes of process control is described. A strip of cinematograph film 35×120 mm. is used instead of a plate. Most of the time saved is in that required for evaluating the line intensity. Three elements in an alloy can be determined in $12\frac{1}{2}$ min.

A Method of Eliminating Calculations in Routine Quantitative Spectrographic Analysis by Means of a

Curved Galvanometer Scale. J. C. Henderson-Hamilton and A. Lourie. (Journal of the Society of Chemical Industry, 1945, vol. 64, Nov., pp. 309-314). A method has been devised whereby the results of spectrographic analysis may be obtained directly in percentages on the special microphotometer reading scale which is described. Hitherto it has been the general practice to use a plain centimetre scale in conjunction with a reflecting galvanometer to obtain microphotometer readings. The readings thus obtained are related to the relative intensities of lines in the spectrum, and hence to concentrations of the constituents of the sample, by some form of mechanical calculator which generally involves the drawing of a density curve. It is found that these intermediate steps can be avoided and much time saved in routine work by the use of a curved scale which accurately represents the relations expressed by the density curve for all types of photographic plate examined.

BOOK NOTICES

AMERICAN WELDING SOCIETY. "*Inspection Handbook for Manual Metal-Arc Welding (Emergency Standard).*" 8vo, pp. iii + 156. Illustrated. New York, N.Y., 1945: The Society. (Price \$1.50.)

This work has been prepared by the American Welding Society's Army Ordnance Advisory Committee to help the inspector and serve as a reliable source of basic information on the factors with which he is likely to have most difficulty.

BATEMAN, A. M. "*Economic Mineral Deposits.*" 8vo, pp. xi + 898. Illustrated. New York, 1942: John Wiley and Sons, Inc.; London: Chapman and Hall, Ltd. (Price 39s.)

This book is about mineral deposits, how they are found, how and where they occur, and what they are. Its chief purpose is as an elementary textbook, but it could be adapted almost equally well to more advanced courses. It is meant to be a source of information also to all those interested in the mineral industry. Its three parts: (I) General Principles and Processes, (II) Ore Deposits, and (III) Nonmetallic Minerals, can be utilized separately or conjointly. It departs from other elementary textbooks in that the heart of the book is devoted to the principles and processes of the formation of mineral deposits.

BROOKING, W. J. "*Arc Welding Engineering and Production Control.*" First Ed. 8vo, pp. xii + 347. Illustrated. New York and London, 1944: McGraw-Hill Book Co., Inc. (Price 24s.)

This deals with control of arc-welded production and is intended to serve as a link between the elementary literature and the highly technical reports of development research. The general factors involved in arc-welded production and the specific means for their control are presented.

GABOR, D. "*The Electron Microscope.*" 8vo, pp. 104. Illustrated. London, 1945: Hulton Press, Ltd. (Price 4s. 6d.)

This monograph is an amplified version of a lecture delivered on March 4, 1943, before the Cambridge University Physics Society. In its present form it intends to be both an introduction to the electron microscope and a critical contribution to its theory. The fundamentals

of electron optics are briefly explained and the instruments described. An appendix on the diffraction theory of the microscope is added.

GALE, W. K. V. "*Soho Foundry.*" 8vo, pp. 49. Illustrated. Birmingham, 1946: W. and T. Avery, Ltd.

This illustrated brochure gives a brief history of the Soho Foundry, Birmingham, which celebrated the 150th anniversary of its opening on January 30, 1946, and the parts played in its development by Matthew Boulton, James Watt, and William Murdoch. In 1895 the business was purchased by W. and T. Avery, Ltd., when the production of steam-engines was gradually discontinued and the Soho Foundry entered on its new career in the manufacture of weighing machinery.

HENSLEY, S. H. "*Optical Instruments in Engineering.*" 8vo, pp. 80. Illustrated. London, 1945: Paul Elek (Publishers), Ltd. (Price 7s. 6d.)

This book outlines the construction and scope of some of the more important optical instruments now in use for workshop purposes and briefly describes the principles upon which they work. The electron microscope is described in principle.

JOHNSON, C. G. "*Metallurgy.*" 8vo, pp. vii + 262. Illustrated. Chicago, 1943: American Technical Society. (Price 17s. 6d.)

The purpose of this textbook is to present in a simple way some of the available knowledge concerning the manufacture and behaviour of ferrous and non-ferrous metals and alloys in use.

JOHNSON, F. "*Metal Working and Heat-Treatment Manual, Vol. 1.*" 8vo, pp. 204. Illustrated. London, 1945: Paul Elek (Publishers), Ltd. (Price 17s. 6d.)

This is the first volume in a series of four to cover the entire range of the heat-treatment of metals. Most authorities have by now recognized the great importance of the subject of metallurgy to engineers, and thus a vital link is being forged between engineers and metallurgists. This book gives a comprehensive and fully up-to-date review of the characteristics of metals and the processes used in

conjunction with them. It is written primarily for the engineer and the student of engineering, but metallurgists will also find it useful and informative.

"*Kingzett's Chemical Encyclopædia. A Digest of Chemistry and Its Industrial Applications.*" Revised and Edited by R. K. Strong. Seventh Edition. 8vo, pp. x + 1092. London, 1945: Baillière, Tindall and Cox. (Price 45s.)

The seventh edition of this well-known work contains many changes and additions.

MARCHANT, SIR JAMES. "*Post War Britain*" with an Introduction by The Rt. Hon. Lord Woolton. 8vo, pp. xv + 240. Illustrated. London, 1945: Eyre and Spottiswoode. (Price 12s. 6d.)

This book contains the following chapters: "The Future Health of the Nation" by Lord Horder; "The Food of the Future" by Sir John Orr; "Building the Homes of the People" by Sir Ernest Simon; "Agriculture" by A. W. Ashby; "The New Chemistry" by E. F. Armstrong; "New Materials—Plastics" by E. G. Couzens; "The Future of Coal" by A. Parker; "Iron and Steel Development" by C. H. Desch; "Railway and Allied Transport" by Sir William V. Wood; "Future Development of Electrification" by J. M. Donaldson; "The Organization of Scientific Research in Great Britain" by Sir Edward V. Appleton.

MARKUS, J., and V. ZELUFF. "*Electronics for Engineers.*" First Ed. 4to, pp. x + 390. Illustrated. New York and London, 1945: McGraw-Hill Book Co., Inc. (Price 36s.)

This is a collection of 142 articles, reference sheets, charts and graphs for design engineers, builders and users of

electronic equipment and component parts, reprinted in convenient form from the pages of "Electronics." This material represents condensed information in graph and chart form which has been in great demand for the reference use of engineers engaged in designing circuits, equipment and individual parts for radio, electronic, television, facsimile, radar, sound, and related vacuum-tube apparatus. The articles and accompanying charts and graphs, carefully edited and arranged in groups, with complete cross-indexing, cover twenty-seven subjects, including audio-frequency impedance-matching networks, antennæ, audio amplifiers, capacitors, cathode-ray tubes, electronic heating, &c.

MAWHINNEY, M. H. "*The Heating of Steel.*" 8vo, pp. vii + 265. Illustrated. New York, 1945: Reinhold Publishing Corporation. (Price 28s. 6d.)

The purpose of this book is to present a practical discussion of those features of heating methods and of furnace tools which are important in obtaining the best results from the heating of steel. It contains the following chapters: I. Chemical Effects of Heating Steel; II. Fuels and Burner Equipment; III. Temperature Distribution and Furnace Control; IV. Heat Transfer and Fuel Economy; V. The Quenching of Steel; VI. Alloys and Refractories; VII. Steel Mill Furnaces.

RITCHEY, J. "*Pattern Making.*" Revised by W. W. Monroe, C. W. Beese, and P. R. Hall. 8vo, pp. 233. Illustrated. Chicago, 1943: American Technical Society. (Price 14s.)

A practical treatise for the pattern maker on wood-working and wood turning, tools and equipment, construction of simple and complicated patterns, modern moulding machines and moulding practice.

BIBLIOGRAPHY

ALTIERI, V. J. "*Gas Analysis and Testing of Gaseous Materials.*" New York, N.Y.: American Gas Association. (Price \$7.50.)

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS. "*Symposium on Stress-Corrosion Cracking of Metals.*" [The papers read at the joint A.I.M.E.-A.S.T.M. Symposium held in New York in November, 1944; with discussions]. 8vo, pp. 500. New York, 1945: The Institute. (Price \$8 foreign; to members of The Iron and Steel Institute \$5.50.)

AMERICAN WELDING SOCIETY. "*Inspection Handbook for Manual Metal-Arc Welding.*" (Emergency Standard). 8vo, pp. 156. Illustrated. New York, N.Y., 1945: The Society. (Price \$1.50.)

BRIGGS, C. W. "*The Metallurgy of Steel Castings.*" 8vo, pp. x + 633. Illustrated. New York and London, 1946: McGraw-Hill Book Co., Inc. (Price 32s. 6d.)

BRITISH STANDARDS INSTITUTION. British Standard 64: 1946. "*Steel Fishbolts and Nuts for Railway Rails.*" 8vo, pp. 15. Illustrated. London, 1946: The Institution. (Price 2s.)

BRITISH STANDARDS INSTITUTION. B.S. 1293: 1946. "*Screen Analysis of Coal (Other than Pulverized Coal) for Performance and Efficiency Tests on Industrial Plant.*" 8vo, pp. 54. London: The Institution. (Price 3s. 6d.)

BRITISH STANDARDS INSTITUTION. B.S. 1295: 1946. "*Tests for Use in the Training of Welders.*" 8vo, pp. 32. Illustrated. London: The Institution. (Price 3s. 6d.)

BRITISH STANDARDS INSTITUTION. STA 5. "*Schedule of Carbon and Alloy Steels. V. Steels, Bars, Billets, Forgings, Plates, Sections, Sheets, Strip, Wire, Tubes.*" December, 1945. 4to, pp. 103. London: The Institution. (Price 7s. 6d.)

BUNN, C. W. "*Chemical Crystallography. An Introduction to Optical and X-Ray Methods.*" Pp. 422. London, 1945: Oxford University Press. Humphrey Milford. (Price 25s.)

COOKE, N. M., and J. MARKERS. "*Electronics Dictionary.*" 8vo, pp. viii + 434. New York and London, 1946: McGraw-Hill Book Co., Inc. (Price 30s.)

DAESEN, J. R. "*Galvanizing Handbook.*" Pp. 130. New York: Reinhold Publishing Corporation.

EVANS, U. R. "*Metallic Corrosion, Passivity and Protection.*" With an Appendix by A. B. Winterbottom. Second Ed. 8vo, pp. xxxiv + 863. Illustrated. London, 1946: Edward Arnold and Co. (Price 50s.)

GABOR, D. "*The Electron Microscope: its Development, Present Performance and Future Possibilities.*" (Electronic Engineering Technical Monographs). 8vo, pp. 104. London, 1946: Hulton Press, Ltd. (Price 4s. 6d.)

GALE, W. K. V. "*Soho Foundry.*" 8vo, pp. 49. Illustrated. Birmingham, 1946: W. and T. Avery, Ltd.

MARCHANT, SIR JAMES. "*Post War Britain.*" With an Introduction by The Rt. Hon. Lord Woolton. 8vo, pp. xv + 240. Illustrated. London, 1945: Eyre and Spottiswoode. (Price 12s. 6d.)

MAUGH, L. C. "*Statically Indeterminate Structures.*" 8vo, pp. viii + 338. Illustrated. New York, 1946: John Wiley and Sons, Inc.; London: Chapman and Hall, Ltd. (Price \$5.)

PARKER, C. M. "*The Metallurgy of Quality Steels.*" Pp. 250. New York: Reinhold Publishing Corporation.

SIMON, W. H. "*American Arc Welding Patents.*" With a Foreword by W. F. Hess. Vol 1. "*Materials, Accessories, Electrodes, Welding Rods, Alloys, Electrode Holders, Welding Shields.*" 8vo, pp. viii + 574. Illustrated. London, 1945: Bailey Bros. and Swinfen, Ltd. (Price £10 10s.)

MINERAL RESOURCES

Rapid Specific-Gravity Method for Estimating the Iron Content of Birmingham, Ala., Red Ores. I. L. Feld, G. D. Coe, and W. H. Coghill. (United States Bureau of Mines, 1946, Report of Investigations 3838). During research on the beneficiation of the iron ores of Birmingham, Alabama, quick assays of the iron content of grab samples were required. Details are given of a simple and rapid method in which the weight of a dried sample and its volume are determined. The specific gravity is calculated and the iron content is read from a curve for the specific-gravity/iron-content relationship.

Swedish Mining Statistics, Collected from Chambers of Commerce Reports. (Jernkontorets Annaler, 1946, vol. 130, No. 4, pp. 161-170). (In Swedish). Seventeen tables are presented giving details, up to and including 1944, of the coal and ores mined in Sweden, and the production of concentrates, briquettes, sinter, pig-iron, charcoal, sponge iron, steel ingots, rolled products, ferro-alloys, and non-ferrous metals.

Tungsten Deposits in Beaver County, Utah. S. W. Hobbs. (United States Geological Survey, 1945, Bulletin No. 945-D). An account is given of the locality, accessibility, geology, and mining history of the tungsten deposits in Utah.

Manganese and Iron Deposits of Morro Do Urucum Mato Grosso, Brazil. (United States Geological Survey, 1945, Bulletin No. 946-A). An account is given of a survey made in 1941 of the manganese and iron ore deposits near Corumbá, Brazil. The manganese deposits were found to amount to about $4\frac{1}{2}$ million metric tons of measured ore with an average content of 45-6% of manganese and 11.1% of iron. Morro do Urucum contains some 1310 million metric tons of

banded hematite material containing about 55% of iron and 20% of silica.

Brazil—Land of Great Potential Mineral Wealth. J. S. Baker. (Mining and Metallurgy, 1945, vol. 26, May, pp. 249-251). Brazil has been one of the most prolific sources for some of the rare minerals needed by the United States in war-time, but small-scale operations and lack of transport hinder development. Depressed mining conditions are likely to follow the end of the war, but the ultimate mineral possibilities of the country are enormous, and await only capital investment and adequate railways and highways.

The Luku Magnetite Deposit, Mienning, Sikang. Y. C. Cheng, K. S. Tsui, T. C. Chow, and H. K. Hu. (Bulletin of the Geological Survey of China, 1942, Apr., pp. 1-6).

Hsiaoching Iron Ore Deposit near Maokupa, Huili District, Sikang. Y. C. Cheng, V. C. Juan, T. C. Chow, and H. K. Hu. (Bulletin of the Geological Survey of China, 1942, Apr., pp. 7-10).

Iron Ore Deposits near Tsienshan, Paihuasu, Huili District, Sikang. Y. C. Cheng. (Bulletin of the Geological Survey of China, 1942, Apr., pp. 11-12).

Iron Ore Deposit of Tsaitukou, Taofu, Sikang. (Y. C. Cheng, K. S. Tsui, and T. C. Chow. (Bulletin of the Geological Survey of China, 1942, Apr., pp. 13-27).

Geology of Kuanyinshan Limonite Deposit, Shui-cheng District, Kweichow. C. J. Peng. (Bulletin of the Geological Survey of China, 1942, Apr., pp. 29-30).

Geology of Paikuowan Coalfield, Huili, Sikang. V. C. Juan. (Bulletin of the Geological Survey of China, 1942, Apr., pp. 31-33).

ORES—MINING AND TREATMENT

(Continued from p. 1 A)

Report on Iron Ore Beneficiation Plants of the Hermann Göring Works, Salzgitter, Germany. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXX-84).

Amine Flotation of Gangue from Magnetite Concentrates. D. W. Scott, A. C. Richardson, and N. Arbiter. (American Institute of Mining and Metallurgical Engineers, 1946, Technical Publication No. 1902). The application of amine flotation to the specific problem of raising the grade of magnetite concentrates has been investigated in the laboratory by both batch and continuous tests. The parts played by the collector, modifier, frother, water, circuit, and grinding are discussed and correlated with the results obtained.

The Recovery of Mineral Products by Flotation from the Waste of Iron-Ore Concentration Plants. Part I. G. G. Bring. (Jernkontorets Annaler, 1946, vol. 130, No. 4, pp. 127-160). (In Swedish). A report is presented on laboratory investigations of the recovery of apatite by flotation from the waste from ore concentration plants at Grängesberg, Malmberget, Luosavaara, and from ores from Nokutisvaara and Andorgöy, and from Tromsö in Norway. Fatty acids were used as the collecting reagents. Apatite floats best at a pH value of 7-9. It sinks slowly in an acid pulp and rapidly in strongly basic pulp. The pH value of the pulp should be controlled by sodium hydroxide additions, but if the ore is low in chloro-apatite and high in hornblende it is necessary to use ammonia. Waterglass is used as a reagent to keep back the gangue. When the raw material is high in mica this tends to float before the apatite, and it is necessary to flocculate the apatite strongly if effective separation is to be achieved; this is done by adding sufficient collecting reagent to bring the apatite above the threshold value. If the pulp is slightly acid or strongly basic the apatite flocculates only slightly or not at all. Results of tests on the effects of the hardness and temperature of the water are given.

Modern Conveying Systems in Steel Plants. L. L. C

Horchitz and P. W. Van Orden. (Iron and Steel Engineer, 1946, vol. 23, Mar., pp. 90-99). A detailed account is given of the material handling systems at the Fontana plant of the Kaiser Company, Inc., and the Geneva plant of the Defense Plant Corporation. The mining, bedding, reclamation, stocking, and con-

veying of the ores, and the design and maintenance of belts and idlers are discussed. Descriptions of a sinter cooling machine and a fully equipped maintenance shop for the splicing of belts by vulcanization are included.

REFRACTORY MATERIALS

Canadian Brucite as a Material for the Production of Basic Refractories. M. F. Goudge and J. G. Phillips. (American Ceramic Society Bulletin, 1946, vol. 25, Mar. 15, pp. 87-92). Following the discovery of brucite limestone in Canada and the development of a process to recover brucite in the form of granular magnesia, a pure magnesia became available for making high-grade basic refractories. This paper gives a brief description of the rock in which brucite occurs; it describes the extracted product, and gives screen and chemical analyses, and the results of petrographic examinations on both the raw and dead-burned materials. Tests indicate that, when properly processed, bricks made from brucite have a refractoriness-under-load comparable to that obtained from the highest grade of dead-burned magnesia commercially available.

Carbon Refractories. (Refractories Journal, 1946, vol. 22, May, pp. 147-151). A description is given of the plant and process for manufacturing carbon refractories at the works of Carblox, Ltd., Loxley, Sheffield. The properties of the carbon bricks, blocks and shapes are: Bulk density 1.52 g./c.c.; approximate porosity 20.6%; cold crushing strength 9500 lb./sq. in.; refractoriness-under-load, no de-

formation at 1710° C. at 50 lb./sq. in.; reversible thermal expansion 0.65% in the 20-1000° C. range.

Some Statistical Methods in Refractory Testing. E. H. M. Badger. (Transactions of the British Ceramic Society, 1946, vol. 45, Jan., pp. 33-43). The interpretation of the results of the testing of refractory materials can only be placed on a rational basis by the use of statistical methods. The application of some of these methods is described.

Refractories for Electric Melting in the Ferrous Foundry. E. K. Pryor and L. R. Burke. (American Foundryman, 1946, vol. 9, Jan., pp. 55-60, 75). The manner in which the conditions in electric furnaces contribute to the wear of the refractory lining is discussed and the suitability of alumina, kaolin, sillimanite, zirconia, and silica refractories for lining these furnaces is considered.

Use of Glazed Coatings to Protect Refractories. R. Newcomb. (Industrial Heating, 1946, vol. 13, Jan., pp. 107-116; Feb., pp. 310-318). The advantages of a refractory coating, sprayed on the inside of furnace walls and then vitrified, as a means of prolonging the life of the lining and preventing the infiltration of air are discussed.

FUEL

(Continued from pp. 1 A-3 A)

Experimental Gas Turbine Operates at 1350 Degrees Fahrenheit. (Steel, 1946, vol. 118, May 6, pp. 134-136, 182-191). An illustrated description is given of an experimental gas turbine capable of developing 3500 h.p. and operating with a gas inlet temperature of up to 1350° F., which was developed by the United States Navy in conjunction with the Allis-Chalmers Manufacturing Company.

Waste-Heat Boilers. W. Gregson. (Journal of The Institute of Fuel, 1946, vol. 19, Apr., pp. 121-130). The fundamentals which determine the main differences in the conception of a waste-heat boiler and a fuel-fed boiler are reviewed, and the advantages and disadvantages of water-tube and fire-tube designs are studied from the viewpoint of waste-heat recovery practice. Ancillary equipment, flue systems, auxiliary firing, sizing of waste-heat boilers, and present and future potentialities are discussed and examples of typical installations described.

The Utilisation of Waste Heat in the Carbonising Industries. J. G. King and F. J. Dent. (Journal of The Institute of Fuel, 1946, vol. 19, Apr., pp. 134-148). The designs of various carbonizing systems are

reviewed from the aspect of waste-heat utilization, and recuperation, preheating of primary air to producers, regeneration, waste-heat boilers, the augmentation of "waste-heat" steam, the dry-cooling of coke, and other developments, are discussed.

Coke-Oven Regenerators. A Study of the Various Considerations to be Taken into Account in the Design of Coke-Oven Regenerators. G. E. Foxwell. (Coke and Smokeless-Fuel Age, 1946, vol. 8, Apr., pp. 73-76; May, pp. 97-99, 102). Calculations applicable to the design of regenerators for coke-ovens are presented and explained. These are based on the findings in the investigations by T. C. Finlayson and A. Taylor (see Journ. I. and S.I., 1946, No. I., p. 58 A).

Coal Washers at Southern Plant Handle 17,000 Tons per Day. W. S. Springer and W. J. McRoy. (Steel, 1946, vol. 118, Apr. 1, pp. 139, 180-186). The evolution of a modern group of coal-washing plants with a combined capacity of 1700 tons/hr. from a small plant of 40 tons/hr. capacity is described. The plants employ a variety of methods and equipment, including breakers and automatic jig-control. Some

of the coal handled has a high inherent ash content, which is sufficiently reduced by washing to render the coal suitable for coking purposes, the already low sulphur content being at the same time further reduced. Loading, water supply, maintenance, sampling, and testing are discussed.

A.G. Sächsische Werke, Böhlen. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXX-13, 1945). This report deals with the low-temperature carbonization plant, the Lurgi high-pressure gasification plant, and the experimental high-pressure Fischer-Tropsch plant at the A.G. Sächsische Werke, Böhlen, near Leipzig.

German Low-Temperature Carbonisation. (Coke and Smokeless-Fuel Age, 1946, vol. 8, Apr., pp. 77-79). Some particulars are given of the larger low-temperature carbonization installations which have been operated in Germany during the war in conjunction with synthetic oil plants.

The Thyssen-Galocsy Complete Gasification Process. (Coke and Smokeless-Fuel Age, 1946, vol. 8, May, pp. 106-107). The operating results achieved with a Thyssen-Galocsy gas producer erected in 1943 at

Wanne-Eickel near Bochum are presented and discussed. The plant was designed to gasify 49 tons of coal per day using oxygen in the producer blast.

Flow Recorders for Steel Works. (Iron and Steel, 1946, vol. 19, May, p. 203). A description is given of a recording flowmeter used in conjunction with an orifice plate; it is suitable for measuring the flow of gaseous fuels and air to metallurgical furnaces.

The Fischer-Tropsch Process. (Combined Intelligence Objectives Sub-Committee, 1945, File Nos. VI-22, X-18, and XV-5). A report is presented on the Fischer-Tropsch plant at Harnes, near Lille, France.

Report of Investigation and Inspection of the High-Pressure Hydrogenation Plant Especially for Brown Coals at Wesseling, near Cologne, Germany. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXVIII-40).

Metallgesellschaft-Lurgi, Frankfurt am Main, Germany. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXXI-23). A report is presented on the oil-production activities in Germany and Japan of companies controlled by the Metallgesellschaft A.G., Frankfurt-am-Main.

PRODUCTION OF IRON

(Continued from p. 3 A)

The Production of Iron in Sweden during the War. G. Sidenvall. (Teknisk Tidskrift, 1946, vol. 76, June 8, pp. 557-560). (In Swedish). Tables and graphs are presented showing the production of iron ores, concentrates, pig-iron, sponge iron, ferro-alloys, and steel ingots in Sweden over the period 1915-1944.

The Education Problem for Ironworks and Mines. K. Josephson. (Teknisk Tidskrift, 1946, vol. 76, May 11, pp. 461-465). (In Swedish). Alternative methods for the technical education and training of young men in industry are discussed with special reference to the organization of technical education by mining and iron-producing companies in Sweden.

The Modern Blast Furnace. T. J. Ess. (Iron and Steel Engineer, 1946, vol. 23, Apr., pp. BF-17-BF-73). A very comprehensive description, with numerous illustrations, diagrams, tables, and graphs, is given of American blast-furnace plant and practice. Details are included of methods of handling, stocking and sintering ore, gas-cleaning, stove and blast control, tapping, and blowing out.

Suppressing Gas Leaks on Blast-Furnace Tops. E. A. Anderson. (Blast Furnace and Coke Association of the Chicago District: Steel, 1946, vol. 118, May 20, pp. 144-147). Methods of reducing gas leaks of blast-furnace-uptake bleeder valves, gauge rods, large and small bells, and gas seal doors are described.

An Experimental Enquiry into the Interactions of Gases and Ore in the Blast-Furnace. Part VI. Influence of Limestone on the Reduction of Iron Ore at up to 850° C. H. L. Saunders and H. J. Tress. (Iron and Steel Institute, 1946, this Journal, Section I). In Part V. of this series (see Journ. I. and S.I., 1938, No I., p. 85 P) the influences of hydro-

gen and steam at 450-850° C. on the reactions taking place in the blast-furnace were studied. In the present paper the effect of limestone (and lime) on the reduction of iron ore by blast-furnace gas is examined under conditions where no interaction occurs between the solids. The temperature range covered is 450-850° C., and equilibrium conditions and reaction velocities are both studied.

At 450-550° C. limestone behaves as a diluent; the same is true concerning lime at 850° C. Lime, however, by absorbing CO₂, accelerates carbon deposition at low temperatures. Up to 750° C., ore reduction predominates and eventually reverses limestone decomposition. At 850° C., limestone decomposition reverses ore deoxidation—these changes occurring when the gas contains about 10% of CO₂. The rates of ore reduction measured at corresponding temperatures and CO₂ concentrations are not appreciably altered by the addition of limestone to the ore.

Manufacture of Sponge Iron in Periodic Brick Kilns. K. M. Smith and S. E. Burton. (United States Bureau of Mines, 1945, Report of Investigations 3841). Tests were made to determine whether sponge iron could be successfully produced in brick kilns at Canton, Ohio. Containers called "saggers" measuring 8 × 8 × 24 in. were made of local fire-clays; these had an average life of ten heats. They were charged with two columns of ore about 20 in. high × 6¾ in. × 2½ in., and packed with anthracite buckwheat mixed with about 15% of ground limestone. Various hematite and magnetite ores were used. In all, 468 tons of sponge iron were produced with a sulphur content usually below 0.02%, and the cost compared favourably with that of imported Swedish sponge iron.

Cemented Steels—A New High-Strength Powder Metallurgy Product. F. P. Peters. (Materials and Methods, 1946, vol. 23, Apr., pp. 987-991). The process of manufacture and the properties of parts made by steel-copper powder metallurgy are described. A porous steel skeleton, pressed from metal powders, is filled up with molten copper. The final product is virtually non-porous and has a high tensile strength. It can be quenched and tempered or case-hardened. This new material is known as "Sinteel G."

General Rules for Powder Metallurgy. H. H. Hausner. (Machinist, 1946, vol. 90, June 1, pp. 290-291). A number of the properties, such as density,

strength, hardness, and electrical conductivity of the products of powder metallurgy are related to factors in the process, such as particle size, pressure, sintering, and temperature.

British Powder Metallurgy. W. D. Jones. (Metal Industry, 1946, vol. 68, May 31, pp. 431-434). The history, development, and commercial future of powder metallurgy in Great Britain are discussed.

Compressed Air Speeds Powder Metal Forming. (Materials and Methods, 1946, vol. 23, Mar., p. 729). A compressed-air traverse for rapidly moving the moulds in the hydraulic presses used for compacting in powder metallurgy is described.

FOUNDRY PRACTICE

(Continued from pp. 4 A-5 A)

Specification, Design and Production of Iron Castings for Vitreous Enamelling. J. W. Gardom. (Institute of Vitreous Enamellers and Institute of British Foundrymen; Foundry Trade Journal, 1946, vol. 78, Apr. 4, pp. 371-375). The design and properties of iron castings are discussed from the viewpoint of the vitreous enameller. The castings should be (1) designed for easy cleaning, (2) clean, sound, and grey, and (3) free from surface defects and internal porosity. The effects of various constituents are reviewed, and suggestions are made as to the compositions desirable for various types of castings.

Cupola Operation and Control. W. W. Levi. (American Foundryman, 1946, vol. 9, Feb., pp. 46-54). Cupola practice at a group of plants producing a wide range of castings is described. Some of the plants concerned are fitted for air-weight control and some for the provision of balanced blast; particulars of these items are given. The following operational factors are discussed: The "lighting-off" of the coke bed; carbon control in front-slagging and intermittent-tapping cupolas; the keeping of proper records of mixtures; weighing and checking of the charge materials; the choice and effects of different cokes; mechanical charging; sampling; the addition of soda ash, zirconium silicide, and ferrosilicon to the metal; and additions to the charge. One plant is equipped for blast-moisture control by means of the lithium-chloride process, the installation being designed for the provision of 13,000 cu. ft. of air/min., at a moisture content of down to 4 grains/cu. ft. In dry weather, as much as 7 grains of moisture/cu. ft. of air can be introduced.

Cupola Operation. D. H. Young. (Institute of British Foundrymen; Foundry Trade Journal, 1946, vol. 78, Apr. 25, pp. 429-432, 439). A detailed review of cupola practice is given, and the factors involved in efficient working with a minimum consumption of fuel are discussed and suggestions made. Formulae for fuel and air calculations, and methods for the determination of tuyere area, depth of bed, &c., are included.

Technical Records in the Foundry. R. D. Lawrie. (Institute of British Foundrymen; Foundry Trade Journal, 1946, vol. 78, Apr. 11, pp. 387-390). The

application of modern control methods to the production of a variety of grey-iron castings is described, and it is shown how it is possible, by keeping careful records of every phase in the production of certain castings, to maintain a high standard of quality. An accurate record of costs, and a permanent record of all manufacturing data are made available; such records are valuable for reference in the event of repeat orders or in the case of failures, and they provide data for the compilation of future estimates or for a study with the object of effecting economies or improvements. Examples of technical records for certain castings manufactured for a variety of uses mainly connected with the recent war effort are included in the paper.

Acicular Iron. (Automobile Engineer, 1946, vol. 36, Apr., pp. 171-172). Details are given of the melting and casting practices developed for making camshafts and crankshafts of a high-strength alloy cast iron containing chromium 0.25-0.6%, molybdenum 0.7-1.2%, and nickel increasing from 1% to 4.5% as the thickness of the part increases from $\frac{1}{2}$ in. to 7-10 in.

Some Notes on Graphitization. L. Crome. (Foundry, 1946, vol. 74, Apr., pp. 99-101, 232-233). Tests to study the factors which influence graphitization during the cooling of malleable cast iron are described. The results indicated that when a white iron casting has been drastically cooled from above 1400° F. it will graphitize in the subsequent annealing treatment much faster than if it had been cooled slowly, and the carbon will be distributed in much smaller nodules.

Mass Production of Tank Wheels in "Black Heart" Malleable. A. B. Bill and J. Peers. (Institute of British Foundrymen; Foundry Trade Journal, 1946, vol. 79, May 23, pp. 75-81; May 30, pp. 113-116). The layout and operation of a plant specifically designed to produce large quantities of a particular casting in high-grade black-heart malleable iron are described, with notes on some of the problems which arose and the steps taken to overcome them.

Recent British Steelfoundry Developments. (Foundry Trade Journal, 1946, vol. 78, Apr. 18, pp. 409-413). Recent developments in the British steel-

foundry industry are reviewed in the notes of a speech delivered by Mr. Brewin during the visit of a mission to Belgium and France. Comparison of the potential production of 150,000 tons for 1938 with the actual production of 360,000 tons for 1943 is made in order to give an idea of the expansion of the industry during the war years. Some of the difficulties encountered are described; the meeting of the ever-increasing demands could only be achieved by the utmost co-operation among producers. The constitution and procedure of the co-ordinating body, the British Steel Founders' Association, are outlined. The three special demands were for bombs, armour castings, and track links, and some of the stringent specifications and tests for these products are mentioned. During the period, several new steels were developed, basic-lined electric furnaces and the alternate cupola-converter method adopted, and a substitute sought for bentonite in green-sand practice.

Technical Considerations Affecting the Production and Use of Steel Castings. A. B. Lloyd. (Journal of the Institution of Production Engineers, 1946, vol. 25, May, pp. 139-163). A comprehensive account of the production of steel castings is given with the object of giving the users an insight into the problems involved in their manufacture and an indication of the defects which may be met with.

The German Steel Casting Industry. C. W. Briggs. (Steel, 1946, vol. 118, Apr. 15, pp. 94-96, 118-120; Foundry, 1946, vol. 74, Apr., pp. 90-95, 137-146). A brief review of German steel-foundry technique is presented with short accounts of the steelmaking practice in acid and basic-lined open-hearth and electric furnaces.

Bessemer Shop Practice. R. Stolle. (Iron and Steel Institute, 1946, Translation Series, No. 276). This is an English translation of a paper which appeared in *Giesserei*, 1942, vol. 29, Dec. 11, pp. 413-419. (See Journ. I. and S.I., 1946, No. I., p. 19 A).

Microscope and Camera in the study of Foundry Sand. A. C. Den Breejen. (American Foundryman, 1946, vol. 9, Feb., pp. 20-26). The opinion is expressed that foundry sand laboratories in general have overlooked the possibilities offered by the microscope and camera, owing to an erroneous conception that complicated and expensive equipment and specialized knowledge are necessary. The principles and technique of microscopy and photomicrography are simply explained and illustrated, and the value of the results to be obtained with inexpensive equipment is emphasized.

The Possibilities of Using Plastics as Core Binders and Their Success in Practice. K. Grassmann. (Iron and Steel Institute, 1946, Translation Series No. 274). This is an English translation of a paper which was published in *Giesserei*, 1943, vol. 30, Nov., pp. 246-253. (See Journ. I. and S.I., 1946, No. I., p. 20 A).

A New Feeding Technique for Castings. T. E. Lloyd. (Iron Age, 1946, vol. 157, Apr. 25, pp. 62-64). A foundry technique is described which enables the size of risers to be considerably reduced. It consists of placing an exothermically reacting compound in the mould at the feed gates. The reaction set up

when it is heated by the metal generates heat, which ensures that the riser solidifies last. As an example, its use for casting steel rolls is described.

Bed Plates—Moulding of Medium Sizes. J. H. List. (Iron and Steel, 1946, vol. 19, May, pp. 195-196). A description is given of the technique for moulding a bedplate about 8 ft. 6 in. long \times 5 ft. 6 in. wide, weighing about 36 cwt.

Making Cast Iron Ingot Moulds. P. Dwyer. (Foundry, 1946, vol. 74, Apr., pp. 84-86, 240-241). An illustrated description is given of the foundry and methods employed by the Bethlehem Steel Company for casting ingot moulds for several of the Company's steel plants.

A Note on the Sources of Hydrogen in Cast Iron. R. C. Tucker. (Foundry Trade Journal, 1946, vol. 79, June 6, pp. 129-132). Trouble was experienced in the centrifugal casting of thin cast-iron cylinder liners owing to bubbles of gas bursting through the inner layer of solidifying metal. This gas was found to be hydrogen, and investigations were made to discover its source. These investigations are described. As long as the moisture content of the coke was not more than 1% no trouble was experienced, but with more than 2% there was a high percentage of scrapped castings. Some notes on the Hatfield and Newell method of determining hydrogen in liquid steel are included.

Investigation of Fried. Krupp, A.G., Blankenburg, Harz. (Combined Intelligence Sub-Committee, File No. XXX-93, 1945). A report is presented on the foundry technique, melting practice, and metallurgical control at the Blankenburg works of F. Krupp A.G.

Krupp A.G. and Bochumer Verein. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXXII-67). A brief account is given of the war-time activities at the Bochum, Hontrop, and Weitmar plants of the Bochumer Verein, together with a longer report of the following items of metallurgical interest at plants of the Krupp Concern: (1) The use of high-grade foreign ore in blast-furnaces; (2) the Renn process for concentrating low-grade domestic ores; (3) the duplex melting processes; (4) forging, including work in the 15,000-ton press; (5) the armour-plate rolling mill; the production of heavy castings and cast armour; and (6) the Krupp research laboratories, now at Wulfrath.

The New Foundry of E. Green & Son, Limited. (Foundry Trade Journal, 1946, vol. 79, June 6, pp. 133-134). A description is given of the new foundry for making parts for Green's economisers. A complete sand-preparation plant is installed and labour is reduced by a monorail for moving the ladles and roller pathways for moving moulds.

Gray Iron Progress through Research. H. F. Taylor. (Gray Iron Founders' Society: Foundry, 1946, vol. 74, Apr., pp. 106, 227-231). A strong plea is made for the organization of more intensive research by iron founders in the United States.

Opportunities for the Foundry Technician in India. J. Blakiston. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 78, Apr. 11, pp. 393-397). The opportunities for the foundry

technician in India and the personal characteristics required are considered. The history, resources, development, economics, climate, and customs of the country are discussed in relationship to the subject.

Foundry Industry and Educational Institutions. A. J. Tuscany. (American Foundryman, 1946, vol. 9, Feb., pp. 60-64). A survey and analysis are given of replies to a questionnaire upon education in foundry theory and practice, drawn up by the Foundry Equipment Manufacturers' Association and addressed to 600 of the leading educational institutions in America. A summary of the present foundry facilities and future needs of educational institutions is given.

Foundry Education and Recruitment. D. H. Ingall. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 79, May 9, pp. 25-29). The changes in the organization of technical education for young people between the ages of 14 and 18 owing to the 1944 Education Act are pointed out, and the steps now being taken to provide foundry education in London are described.

Apprentice Training in the Foundry. J. B. Longmuir. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 79, May 16, pp. 55-59). A detailed description is given of the training scheme which has been organized for foundry apprentices by Newton Chambers & Co., Ltd.

Modernization of Foundries. L. B. Knight. (American Foundrymen's Association: Foundry, 1946, vol. 74, Apr., pp. 88-89, 220-222). Methods of modernizing the organization, procedures, costing, equipment, and working conditions in large foundries are discussed.

Ventilating the Mold Shakeout. C. C. Hermann. (Foundry, 1946, vol. 74, Apr., pp. 104-105, 210-215). Equipment for removing dust and fumes from the knocking-out department of large foundries is described and illustrated.

Dust Collectors. (Iron and Steel, 1946, vol. 19, May, pp. 185-187). A description is given of a dust collector suitable for swing grinding machines used for grinding billets and castings.

Rapid Test for Fluidity Measurement. G. B. Taylor. (Iron Age, 1946, vol. 157, Apr. 11, pp. 62-63). A modification of the standard spiral fluidity test in the foundry is described. The modification is designed to simplify the making of the spiral mould and to eliminate undesirable time-lag in obtaining a reading.

Some Casting Troubles. J. L. Francis. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 79, May 30, pp. 103-111). Examples of defects in ferrous and non-ferrous metal castings are described and illustrated and suggestions for their prevention are made.

PRODUCTION OF STEEL

(Continued from pp. 5 A-7 A)

Ferrous Production Metallurgy Plants Reconverted to Peacetime Operation Make Use of War Discoveries. H. K. Work and H. B. Emerick. (Mining and Metallurgy, 1946, vol. 27, Feb., pp. 86-88). The application of war-time developments in the American iron and steel industry to peace-time usages is discussed with special reference to raw materials, blast-furnace practice, sponge-iron production, open-hearth practice, slag-metal controls, the Bessemer process, electric furnaces, and alloy steels.

Iron and Steel Process-Metallurgy Practice Gradually Returning to Normal—Improvement Varied but Minor. M. Tenenbaum. (Mining and Metallurgy, 1945, vol. 26, Feb., pp. 82-86). In a review of the process-metallurgy of iron and steel during 1944, a few of the numerous factors involved in the maintenance of the war-time production programme at the level necessary to accomplish the enormous outputs obtained are discussed.

Modern American Steelworks Practice. W. F. Cartwright. (Proceedings of The South Wales Institute of Engineers, 1946, vol. 61, pp. 217-258). A comprehensive and detailed report of organization, equipment, and practice in modern American iron and steel works is given in a survey written as a result of a visit to America and Canada in 1945 to investigate the manufacture of wide strip.

Practical Application of Statistical Methods in a Quality Control Program. W. T. Rogers. (American Society of Metals: Blast Furnace and Steel Plant,

1946, vol. 34, Feb., pp. 233-235). The value of statistical methods in industry in general and in steel plants in particular is pointed out. Frequency distribution, control chart, simple correlation, and multiple correlation methods are discussed. In dealing with operations such as exist in steel plants, close co-ordination of control charts and correlation is necessary if a control programme is to develop its maximum efficiency.

Research Organization in the Iron and Steel Industry. C. F. Goodeve. (British Steelmaker, 1946, vol. 12, May, pp. 222-225). The history of research in the British iron and steel industry is briefly traced, and the functions of the British Iron and Steel Research Association are explained.

Problems Involved in Starting up an Iron and Steel Plant. (Steel, 1946, vol. 118, May 6, pp. 166-170, 180). The steps taken in the closing down and starting up of an iron and steel works are described.

Air Blowers for Steelworks. N. Mear. (British Engineering Export Journal, 1946, vol. 28, May, pp. 917-919). Illustrated descriptions are given of twin-impeller blowers of the Roots type which have been designed for supplying air to cupolas, converters, and rotary furnaces.

The Swedish Acid Open-Hearth Process. S. M. Wejle. (Metallurgia, 1946, vol. 33, Apr., pp. 315-317). Some reasons why Swedish acid open-hearth steel is of such a high quality are given and some of its applications are mentioned.

Arc Furnaces. J. Lewis. (Iron and Steel, 1946, vol. 19, May, pp. 183-184). The requirements of the control of the supply of current to arc furnaces are outlined, and a method of automatic control is described.

The Making of Electric Furnace Alloy Steels. W. J. Reagan. (American Society for Metals: Blast Furnace and Steel Plant, 1946, vol. 34, Feb., pp. 236-240; Mar., pp. 345-349, 354). An over-all picture of the many various steps in the production of electric-furnace alloy steels is given, and the advantages of the basic electric-furnace process are enumerated. The particular furnaces discussed are of the swing-roof, top-charge type, with shell diameters of 16 and 17 ft. and charging capacities of 85,000 and 110,000 lb. Production with all-cold charging ranges from 8 to 12 tons/hr., and can be increased to as much as 20 tons/hr. by means of the duplex and triplex processes, which are described. Teeming, stripping, processing, testing, and finishing are also discussed.

Coreless Induction Furnaces. M. J. Marchbanks. (Institution of Electrical Engineers, 1946, Preprint). The paper deals mainly with induction furnaces for

steel melting, although attention is also given to other applications such as the case-hardening of steel. Construction of furnace bodies to avoid heating of the metal framework, and the fritting of refractory linings *in situ* are discussed. Other apparatus in the furnace circuit, such as high-frequency generators, methods of switching condensers, and the protection of the generator, is described. The changing characteristics of furnaces due to changes in the physical properties of the charge are discussed. In an appendix it is shown how to calculate the temperature distribution through a cylindrical surface receiving energy at a uniform rate per unit area.

Slags in Acid Electric Steelmaking. C. C. Wissmann. (Metal Progress, 1946, vol. 49, Apr., pp. 735-738). This paper can be regarded as a supplement to an earlier paper by the same author ("Final Additions to an Acid Electric Heat," Journ. I. and S.I., 1946, No. I., p. 41 A). Methods of estimating the FeO contents of the metal and slag by the colour of the slag and by the Herty viscometer, and the effect of making limestone additions when the boil is beginning to subside are dealt with.

FORGING, STAMPING, AND DRAWING

(Continued from pp. 7 A-8 A)

The Development of Hydraulic Presses. E. Müller. (Zeitschrift des Vereines deutscher Ingenieure, 1942, vol. 86, Oct. 3, pp. 591-596). The development of heavy hydraulic presses is reviewed and several types are described and illustrated.

Power Hammers. D. L. Perry. (British Engineering Export Journal, 1946, vol. 28, May, pp. 911-916). Recent developments in British pneumatic hammers are reviewed.

Steel Propeller Blade Development at V.D.M., Hamburg. (British Intelligence Sub-Committee, 1945, Final Report No. 321: H.M. Stationery Office). Work done on the development of hollow steel propeller blades for aircraft by the forging and welding of chromium-manganese-vanadium steel is described.

Manufacture of German High Explosive Shell Steel for Artillery. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXIX-27). Notes are submitted on the forging and machining of high-explosive shells in Germany.

Forging Die Design. J. Mueller. (Steel Processing, 1946, vol. 32, Feb., pp. 116-118). The use of the upright helve hammer for forging automobile gear control levers is described with notes on the design of the forging dies.

Designing, Drafting, and Using Press Tools. C. W. Hinman. (Steel Processing, 1946, vol. 32, Feb., pp. 110-115). The design of press tools for cutting shaped blanks out of steel strip is discussed and illustrated by an example. The method of determining the most economical layout and width of strip are explained.

Improving Forming Processes by Phosphate Coatings. A. Durer, E. Schmid, and H. D. Graf von Schweinitz. (Zeitschrift des Vereines deutscher In-

genieure, 1942, vol. 86, Jan. 10, pp. 15-18). It is well known that forming operations, drawing in particular, are made easier when the steel has a phosphate coating.

Laboratory tests in the drawing of steel tubes to discover the reasons for this are described. The good adhesion and the oil-adsorption properties of the coating were found to be main reasons.

Greatly Increased Use of Stainless Steel Stampings Predicted. (Steel Processing, 1946, vol. 32, Feb., pp. 104-105, 133). Illustrated descriptions are given of various articles made of pressed and drawn stainless steel sheet. Hatch covers for ships made of assembled stampings, and kitchen utensils made in one and two pieces, exemplify the wide range of articles which are now made of stainless steel in the United States.

Machine Built with Manifold Dies Points Steel Tubes. (Steel, 1946, vol. 118, Apr. 1, pp. 141, 209). The pointing of ferrous tubes by means of hydraulically operated dies preparatory to cold-drawing is discussed. It is claimed that, by the method described, production at some plants has been increased by 100% with 50% less labour and that the die stroke is synchronized and pickling facilitated.

Detroit Seamless Steel Tubes Co. Has for 45 Years Manufactured Steel Tubes. C. Longenecker. (Blast Furnace and Steel Plant, 1946, vol. 34, Feb., pp. 231-232). Plant and methods for the manufacture of high-quality steel tubes from $\frac{1}{4}$ in. to $5\frac{1}{2}$ in. in dia. and from 24 B.W.G. to $\frac{1}{2}$ in. in wall thickness are described.

Carbide Die Applications, Present and Future. E. Glen. (Iron Age, 1946, vol. 157, Apr. 25, pp. 51-54). Some applications of carbide dies which were

kept secret during the war are now published. These include deep-drawing dies $13\frac{1}{2}$ in. in dia., dies for nosing 105 mm. artillery shells, and the drawing of steel tubing to a wall thickness of 0.010 in.

Fine Wire Drawing. S. C. Avallone. (Iron Age, 1946, vol. 157, Apr. 11, pp. 64-65). War-time demands for fine steel wire necessitated sharp increases in the output of this item and confronted American wiremakers with new problems, which are discussed. The technique now used in America for the successful production of fine wire on a large scale is described, and potential post-war markets are reviewed.

Diamond Dies for Wire Drawing. C. K. Wall. (Materials and Methods, 1946, vol. 23, Mar., pp. 717-719). The manufacture of wire-drawing dies is briefly described by ten illustrations and diagrams with explanatory notes.

The Crum Calculator for Wire Drafting. E. J. Crum. (Wire and Wire Products, 1946, vol. 21, Mar., pp. 221-223, 253-254). A small and simple calculating device for wire-drawers is described and its use is explained with examples. With its aid, problems relating to the number of holes, the percentage draft per hole, the total reduction of area and intermediate die sizes can be rapidly solved.

Wiredrawing Machines—Past, Present, and Future. N. Davidson. (Wire Industry, 1946, vol. 13, Apr., pp. 211-214, 230). Improvements in the type and design of wire-drawing machinery which have been introduced since 1930 are reviewed. More research is advocated and the importance of control in the preparatory cleaning and liming processes is stressed.

New Marshall Richards Non-Slip Model Multiple Hole High-Speed "Pacemaker" Wire Drawing Mach-

ine. (Wire Industry, 1946, vol. 13, May, pp. 265-267). High-speed wire-drawing machines, equipped with from two to nine blocks, each block independently driven by a variable-speed D.C. motor, are described. The fastest machines can finish wire at up to 2000 ft./min. The wire, as it runs from one block to the next, passes over a spring-loaded swinging arm which automatically adjusts the speed of the motor driving each block, causing it to run without slip at exactly the speed required.

The Maintenance of a Steel Wire Mill. C. B. Tolputt. (Wire Industry, 1946, vol. 13, May, pp. 269-271). The organization of maintenance in a steel wire mill is described. The causes of breakdowns are analysed into failure of lubrication, overloading, or corrosion. The plant in question is built up on the unit principle; each unit is driven by a separate motor, and several similar units make up a machine. This system facilitates maintenance, permits the standardization of parts and reduces the number of spares to be kept in stock.

History and Development of the Indian Wire Industry. (Wire Industry, 1946, vol. 13, May, p. 273).

Wire Rope Forms. (Wire Industry, 1946, vol. 13, Apr., pp. 217-219). To provide producers of rope wire with information on the ultimate finish of their products a summary is given of the main British grades of wire ropes. Four main types of wire rope are fabricated in Great Britain. These are: (1) Round strand construction; (2) flattened strand construction; (3) multiple construction, flat strand, non-rotating; and (4) locked coil construction. Illustrations of the sections of these types are given.

ROLLING-MILL PRACTICE

(Continued from p. 8 A)

Power Steel Maker Modernizes Power System. A. D. Howry and R. H. Wright. (Iron and Steel Engineer, 1946, vol. 23, Apr., pp. 69-72). A description is given of improvements made by the Alan Wood Steel Company to the electric power system supplying current to their rolling mills.

Development and Application of Twin Motor Drive. G. E. Stoltz. (Iron and Steel Engineer, 1946, vol. 23, Mar., pp. 62-67). The development, application, and advantages of twin motor drives for rolling mills are discussed, and some specialized installations are described and illustrated. The increased use of this type of drive in the steel industry is predicted.

Applying Fluid Drive in Industry. G. V. Edmonson. (Iron and Steel Engineer, 1946, vol. 23, Mar., pp. 73-82). The principles of fluid drive are discussed, and examples of its application in the steel industry are described.

The Spraying of Gear Lubricants. D. E. Whitehead. (Iron and Steel Engineer, 1946, vol. 23, Mar., pp. 68-72). The application of lubricants by spraying is described, with special reference to the lubrication of open gearing. The advantages of the method are discussed, and particulars of tests are given.

Grease Lubricants. J. C. Van Gundy. (Steel, 1946, vol. 118, Mar. 25, pp. 92-95, 111-118; Apr. 1, pp. 142-145, 188-208). A summary of the purpose and effects of the ingredients of grease lubricants is given. The many types of commercial greases are classified into seven groups, and the method of manufacture, uses, properties, characteristics, and critical factors of each group are discussed.

The Sendzimir Precision Cold Strip Mill. T. Sendzimir. (Iron and Steel Engineer, 1946, vol. 23, Apr., pp. 53-59). The principles of the Sendzimir cold strip mill are explained. In this mill the work rolls are very small in diameter, e.g., mills for strip 50 in. in width have work rolls only $2\frac{1}{4}$ in. in dia. These work rolls are not supported by backing rolls in the usual way, but are surrounded by four intermediate rolls backed by castors. The castor bed consists of a number of evenly spaced pillars each with a castor on top; these pillars are firmly bolted to the mill housing. The intermediate rolls therefore only transmit the load from the work rolls to the castors which in turn transmit it through the castor supports to the solid steel mill housing.

"Flying Mike." (Steel, 1946, vol. 118, Apr. 22, pp. 87, 135). An illustrated description is given of a

"flying" micrometer with a throat 10 in. deep which enables accurate thickness measurements to be made up to the centre of steel strip 19 in. wide.

Some Observations on Seamless Tube Making. N. Hamilton. (Iron and Steel Engineer, 1946, vol. 23, Mar., pp. 55-61). Various designs of piercing mills, and some of the factors necessary for the production of sound steel for the making of seamless steel tubes, are discussed. The melting-shop layout, equipment, and practice at the Beaver Falls plant of The Babcock and Wilcox Tube Company are

described and illustrated, and the value of accurate observation and recording of shop data, and of co-ordination between the melting shop and the mill, is emphasized.

Mechanical Cooling Beds for Rolling Mills. H. Hoff. (Zeitschrift des Vereines deutscher Ingenieure, 1941, vol. 85, Apr. 12, pp. 361-366). The general requirements of cooling beds for rolling mills with high outputs are discussed and several modern installations are described and illustrated.

HEAT-TREATMENT

(Continued from pp. 9 A-10 A)

Car-Type Furnaces. (Steel, 1946, vol. 118, Apr. 29, p. 93). A description is given of a large car-bottom furnace for stress-relieving tanks and pressure vessels. It is 15 ft. 2 in. wide \times 65 ft. long and is 18 ft. 2 in. high from the floor of the car.

Heat Treating Furnace Features Automatic Work Cycle. (Steel, 1946, vol. 118, May 13, p. 121). A description is given of a gas-fired heat-treatment furnace for lorry rear-axle housings. It is designed to heat the housings to 1650° F. in 48 min. and to hold them at that temperature for 1 hr. Each housing is on a separate tray and a clock controls the pusher mechanism so that the cycle of operations is automatic.

Industrial Heat Treating Furnaces in Germany. (British Intelligence Objectives Sub-Committee, 1945, Fiat Final Report No. 434: H.M. Stationery Office). Descriptions are given of German heat-treatment furnaces and installations. A great number of electric and gas-fired salt-bath furnaces are used for a wide temperature range. Recuperators are used to a large extent on fuel-fired furnaces.

Heat Treating and Galvanizing Performed in Commercial Metals Treating Co. Plants. (Industrial Heating, 1946, vol. 13, Feb. pp. 323-332; Mar., pp. 512-520). A description is given of the heat-treatment and galvanizing furnaces, tanks, and equipment at the works of the Commercial Metals Treating Company.

An Examination of Slow Cooling Methods. J. W. Barber and E. R. Cole. (Iron and Steel Engineer, 1946, vol. 23, Mar., pp. 84-88). Methods of slow cooling are reviewed, and the design and arrangement of cooling pits for various heat-treated products are discussed.

Improving the Formability of NE 8630 Steel Sheet. J. L. Waisman and W. T. Snyder. (Metal Progress, 1946, vol. 49, Apr., pp. 755-760). When a change-over was made from steel S.A.E. 4130 to N.E. 8630 (a low-alloy chromium-nickel-molybdenum steel) for making certain parts for aircraft by cold-forming, considerable trouble from cracks was experienced. An account is given of the investigation of four heat-treatments which was carried out and of the measures taken which overcame the difficulty.

Observations on the Impact Strengths of Alloy Steels Hardened from Cyanide Baths. S. M. Lenhoff and

L. F. Roth. (Metal Progress, 1946, vol. 49, May, pp. 960-967). An investigation of the failure with a brittle fracture of rollers made of case-hardened low-alloy steels (in particular, a chromium-vanadium steel) is reported. A form of impact test was devised and the number of blows to fracture was taken as the criterion of the toughness. Case-hardening in solid, liquid, and gaseous media was tried. Hardening in a molten cyanide bath always gave the lowest impact strength. The best results were obtained on the chromium-vanadium steel by carburizing at 1650° F. in either a solid or a gaseous medium, cooling slowly, reheating in a controlled atmosphere, quenching in oil, and tempering for 1 hr. at about 650° F.

Gas Carburizing. (Metallurgia, 1946, vol. 33, Apr., pp. 317-319). The equipment and layout of a gas-carburizing plant are described. This is a controlled atmosphere plant developed to manufacture from town gas a hydrocarbon diluent or carrier gas which alone supplies a protective atmosphere for heating and cooling steel without detriment to surface finish.

Atmosphere Calibration for Heat Treating Airplane Propellers. C. A. Liedholm. (Metal Progress, 1946, vol. 49, Apr., pp. 744-749). In a previous paper details were given of two furnaces for the heat-treatment of hollow steel propeller blades for aircraft (see Journ. I. and S.I., 1946, No. I., p. 77 A). In the present paper the methods of controlling the heat-treatment atmosphere so as to prevent surface decarburization are described.

Flame-Hardening Setup for Small Machined Parts. W. B. Sharav. (Welding Journal, 1946, vol. 25, Apr., p. 328). A description is given of a flame-hardening machine for hardening gears, rollers, wheels, and small circular parts in which the part is spun while being heated by radially positioned oxy-acetylene burners.

Induction Hardening Steam Hammer Piston Rods. (Steel, 1946, vol. 118, Mar. 25, pp. 121, 142). The surface-hardening of steam-hammer piston rods in a vertical induction heat-treating apparatus is described, and the effects of the treatment are discussed. In one test an induction surface-hardened rod served for 598 hr., compared with an average working life of 210 hr. for the conventional-type rod, in another test the figures were 434 hr. and 254 hr., respectively.

Induction Heat-Treatment of Internal Surfaces as Applied to Automotive Industries. H. E. Somes. (S.A.E. Journal, 1946, vol. 54, Feb., pp. 45-54, 63). The use of induction heat-treatment combined with precision quenching, particularly where only a portion of the product requires selective treatment, was one of the major applications of new processes made during the war. The application of the process to problems in the automobile industry is discussed and a number of products to which use of the process may be extended are suggested. An account is given of the experiments which were conducted in the development of the process, and of its application to the selective heat-treatment of the Ford passenger-car hub; by means of this application an integral bearing race was provided by bore hardening. Present applications of the technique to the use of static and progressive cylinder heat-treating machines are described.

Quenching Water Requirements of Induction Heated Parts. B. R. Miller. (Metal Progress, 1946, vol. 49, Apr., pp. 750-752). An account is given of tests undertaken to determine the quantity and pressure of water, and the quenching time required when induction-hardening large and small parts such as crankshaft bearing surfaces, gear drives, track pins, and track roller assemblies.

How to Design Coils for Induction Heating. F. W. Curtis. (Machinist, 1946, vol. 90, May 18, pp. 201-204).

Controlled Low-Temperature Stress Relieving. T. W. Greene and A. A. Holzbaur. (Welding Journal, 1946, vol. 25, Mar., pp. 171-S-185-S). The residual stresses in important welds in ship construction are analysed and investigations of their magnitude and of methods of relieving them are reported. A detailed description is given of a successful technique for relieving them. It consists of passing two multiple oxy-acetylene burners along the plates in such a manner that the weld seam is only warmed while the parent plate on each side is heated to about 350° F. The equipment for applying this treatment on the outside and inside of hulls is described and illustrated.

Shrinking and Hardening Track Rollers in One Operation. (Machinery, 1946, vol. 68, Apr. 25, pp.

521-525). Large economies in time and labour have been effected by an application of the Tocco induction-hardening process in which two rollers and a hub are assembled together to make up track rollers for bulldozer tractors. After expansion by heating to a high temperature, the rollers are shrunk on the hub and, as the shrinkage occurs, the roller treads and the outside surfaces of the roller flanges are simultaneously hardened by a copious water quench directed on the entire circumference of the rollers.

Rapid Hardening. H. Ruhfus and J. Klärding. (Zeitschrift des Vereines deutscher Ingenieure, 1941, vol. 85, May 24, pp. 486-487). A rapid method of hardening (*Tauchhärtung*) is described in which the part is placed for a short time in a molten salt or metal bath at well above the hardening temperature; when the surface, but not the core, has been heated above the transformation point the part is withdrawn and quenched. For small parts the heating time is very short, usually less than 1 min. Data on the depth of hardness obtained in different baths and the heating times are given.

Subzero Treatment Simplifies Hardening of Alloy Carburizing Steels. H. E. Boyer and H. C. Miller. (Materials and Methods, 1946, vol. 23, Mar., pp. 730-734). The effect of sub-zero temperature treatment on the hardness and stability of carbon and low-alloy carburizing steels was determined by tests. The sub-zero treatment should be applied as soon as possible after quenching and before tempering. Repeating the sub-zero treatment had no beneficial effect. The treatment proved to be just as beneficial with these steels as it has been with high-speed steels.

Quenched Steel Castings. C. W. Farrar. (Canadian Metals and Metallurgical Industries, 1946, vol. 9, Mar., pp. 37-38). The development of the practice of quenching and tempering steel castings in the United States and Canada is outlined and data on some of the properties obtained by this treatment are given.

Hot Oil Quenching. D. C. Miner. (Steel, 1946, vol. 118, Apr. 29, pp. 88-89, 118-121). Some examples are given of successful applications of the practice of quenching steel in oil held at 300-350° F.

WELDING AND CUTTING

(Continued from pp. 10 A-11 A)

Arcwelding Equipment in Wartime Germany. F. W. Myers, jun. (Iron Age, 1945, vol. 157, Apr. 25, pp. 46-50). Descriptions are given of automatic and semi-automatic methods of welding which were developed in Germany during the war. In addition to spot-welding at medium frequencies and atomic-hydrogen welding, four other procedures are briefly described, these are the Elin-Hafergut, the Kama, the Kaell, and the Ellira.

"Exchange"—Repair of a Heavy Crane Wheel by Welding. H. Hüngsberg. (Elektroschweissung, 1940, vol. 11, Dec. pp. 189-191). After successfully resurfacing the tyre of a heavy crane wheel, cracks

were discovered in the main body of the wheel. The cracked inner part was removed by flame-cutting and replaced by a fabricated part which was then rewelded to the tyre thus avoiding the loss of the latter. Distortion was completely avoided by the application of a simple clamping jig.

Equipment for Preheating and Stress-Relieving Welded Constructions. W. T. Schneider. (Elektroschweissung, 1940, vol. 11, Nov., pp. 180-184). High-tensile steel structures can be welded satisfactorily provided that the proper welding procedure is applied. In addition to correct electrode types and diameter, preheating and post-heat-treatment

plays an important part. A number of gas-fired furnaces which can accommodate large constructions are described.

The Calculation of Overhead-Charges in the Welding Shop. A Schmidt. (Elektroschweissung, 1940, vol. 11, Oct., pp. 158-162). The normal calculation of the costs based on the price for the material plus wages and overheads is also generally used in the electric welding shop. An examination of the various types of welded joints showed that electrode costs and current consumption influence the overheads of a welding shop considerably. These two factors vary appreciably according to the thickness of the plates to be welded and it is therefore suggested that instead of a fixed charge, a scale of overheads based on a range of plate thicknesses should be used.

Tensile Tests on Steel Bars (St 52) Longitudinally Welded by the Ellira Process. K. Albers. (Elektroschweissung, 1940, vol. 11, Nov., pp. 174-180). A great number of tensile tests had been carried out on bars which had been longitudinally welded by the Ellira process (German name for the Unionmelt process), in order to ascertain the suitability of this process for highly stressed structures of high tensile steel (St 52). The results of the investigation, which also included hardness measurements, metallographic examination and the calculation of shrinkage stresses, are compared with similar welds made by hand.

The micrographic examinations showed the cast structure of the weld zone and a large zone of fusion with a smaller increase in hardness than that obtained by hand welding. The tensile strength and the elongation of the weld metal were sufficient. Tensile tests on the welded bars gave good results regarding strength even without heat-treatment. The shrinkage stress was well below the yield stress of the parent metal.

The Electric-Arc Welding of Thick Plates. K. Jurczyk. (Elektroschweissung, 1940, vol. 11, Sept., pp. 146-152). In order to keep shrinkage and distortion as low as possible when welding thick plates, small gaps of appropriate form and preheating are recommended.

Dimensional Changes during Welding and Stress-Relieving. E. Gerold and A. Drozd. (Elektroschweissung, 1940, vol. 11, Sept., pp. 141-146). The dimensional changes during welding and subsequent annealing for stress-relieving were investigated. The authors show that, because of the inherent connection between stress reduction and dimensional changes, the residual shrinkage stress in parts which have been stress-relieved is only 50% of the original value.

The Influence of the Welding Conditions on the Deformation of Girders in Off-Centre Welding. R. Malisius. (Elektroschweissung, 1940, vol. 11, Aug., pp. 131-136). Longitudinal welds away from the axis of a girder are apt to bring about deformation, shrinkage and residual stresses. The author describes tests carried out to ascertain the influence of the welding conditions such as heat input, electrode size, and number of runs, with a view to predicting the magnitude of the final distortion and residual stress.

Magnetic Inspection of Welds. G. C. Close. (Steel Processing, 1946, vol. 32, Feb., pp. 122-125). Recommendations are made on the use of the magnetic powder process for the inspection of welds. Examples of defects and powder indications on welds in chromium-molybdenum steel aircraft parts are illustrated and discussed.

Material Transmission in the Welding Arc. H. v. Conrady. (Elektroschweissung, 1940, vol. 11, July, pp. 109-114). The author attempts to explain the phenomenon of material transmission in the electric arc with the help of a new hypothesis. According to this, the transfer of material is mainly due to a mechanical force which acts on the cathode spot. The molten material of the electrode end is set into oscillating motion by it until the movement becomes large enough and the molten material touches the work piece. A short circuit takes place and the arc is extinguished; the "pinch effect" and surface tension of the molten pool complete the transfer of the drop.

Annealing Welded Joints in Pipelines. A. W. Isermann. (Elektroschweissung, 1940, June, vol. 11, pp. 99-102). The annealing of welds on site, especially of high pressure pipe lines, is simplified by using a mobile electric resistance heater which is described in the article. The advantages claimed as compared with gas-fired heaters are: shorter heating time, easy handling, exact control of the whole process, and lower cost.

Recent Improvements in the Design of Extruding Presses for Welding Electrode Coatings. R. Müller-Börner. (Elektroschweissung, 1940, vol. 11, June, pp. 97-99). Experience has shown that any alteration in the direction of the flow of plastic materials increases the resistance. The application of higher pressure for extruding has the disadvantage that the constituents of the coating material show a tendency to segregate and the moisture of the binder is squeezed out. By altering the shape of the extruding nozzle in such a way that the flow of the coating material is nearly in the same direction as the wire feed, higher extruding speeds and better results were obtained.

The Influence of Cooling on the Weld Quality. C. Stieler. (Elektroschweissung, 1940, vol. 11, June, pp. 93-97; July, pp. 115-117). A series of tests are described, their purpose being to ascertain the effect of water-cooling during welding on the mechanical and physical properties, the microstructure and the cost of metallic-arc and atomic-hydrogen welds. The parent metals used were steels: St 34 (carbon 0.09%, silicon 0.05%, manganese 0.40%, phosphorus 0.01%, sulphur 0.02%, copper 0.11%); St 55 (carbon 0.13%, silicon 0.05%, manganese 0.50%, phosphorus 0.02%, sulphur 0.03%); St 52 (carbon 0.16%, silicon 0.91%, manganese 1.0%, phosphorus 0.02%, sulphur 0.05%, copper 0.29%). The mechanical and physical properties of such welds showed a marked decrease in the impact strength and the bending angle. The hardness of the plates welded with artificial cooling during the process increased considerably. The microstructure of metallic-arc welds was hardly affected by the cooling, whereas the atomic welds showed coarse grain

structures. The author recommends artificial cooling in practice only in exceptional cases.

Welding Jigs for Steel Structures. W. T. Schneider. (Elektroschweissung, 1940, vol. 11, May, pp. 82-86). A number of welding jigs and manipulators for large parts, mainly girders, which have proved successful in practice are described. Considerable saving in man-hours can be achieved by using them. A combined clamping and travelling gantry for two automatic welding heads working simultaneously has proved useful and saved extensive straightening operations after welding.

Test Welds for Welding Instructors. T. Krakat. (Elektroschweissung, 1940, vol. 11, May, pp. 86-90). Eighteen test welds which have to be made by welding instructors are described and the best method of making them is explained.

Welding of Manganese Steel. K. L. Zeyen. (Elektroschweissung, 1940, vol. 11, May, pp. 78-81). The application of heat to manganese steel of the following composition: 1.20-1.4% of carbon, 12-15% of manganese, less than 0.35% of silicon, less than 0.08% of phosphorus and less than 0.035% of sulphur, is likely to destroy the austenitic structure of the steel. Resurfacing by welding this type of steel must therefore be done with certain precautions, such as lowest possible current, cooling, and the use of appropriate electrodes. Rods of the following composition are recommended: 0.97% of carbon, 0.34% of silicon and 13.6% of manganese.

Recent tests have shown that manganese steel electrodes are not suitable for butt and fillet welds on manganese steel, but good results were obtained with chromium-nickel rods. This type of electrode gave good and ductile weld seams without disturbing the austenitic structure of the parent plates.

Welded Gear Wheels and Gear Boxes. H. Schmidt. (Elektroschweissung, 1940, vol. 11, May, pp. 73-77). Gear wheels fabricated in rolled steel, compared with cast wheels, are lighter and show better utilization of material. By using mild steel for wheel centres and steel of 60-85 kg./sq. mm. tensile strength for the rims a saving of 25-35% in weight can be achieved.

Metallographic and mechanical tests have proved that the best results can be obtained by preheating the rims to a temperature of 180-200° C. and subsequent welding at that temperature.

Fabrication of gear boxes by using rolled plates and scrap material is cheaper than cast designs and results in even higher savings of weight. A number of interesting designs and the recommended fabrication procedures are described.

Metallurgy of Aircraft Welding. R. Smallman Tew. (Transactions of the Institute of Welding, 1946, vol. 9, Apr., pp. 47-50). The oxy-acetylene and atomic-hydrogen welding, as well as arc, spot, and flash welding and furnace-brazing of aircraft landing-gear parts are discussed.

Processing and Fabrication of Stainless Steel Sheet and Plate Products. Part V. Joining of Chromium-Nickel Materials. H. S. Schaufus and W. H. Braun. (Steel Processing, 1946, vol. 32, Feb., pp. 106-109, 126). The technique for the oxy-acetylene welding of

stainless steel is described with notes on joint design, welding rods, jigs, and clamps.

Three Coatings for Stainless Steel Welding Electrodes. O. J. Barnett. (Steel, 1946, vol. 118, Mar. 25, pp. 98-100, 148-149). War-time requirements and research established "AC-DC" as another basic coating for stainless-steel welding electrodes. Tests are described in which lime, titania, and AC-DC coatings are compared. The opinion that the AC-DC will take the place of the titania coating is expressed.

Oil Refinery Pressure Vessels. E. P. S. Gardner. (Welding, 1946, vol. 14, Apr., pp. 150-155). A critical survey is presented of American methods for the arc-welding of corrosion-resistant linings of oil refinery pressure vessels. The types of lining and the various means of assembly are discussed.

Welded Pressure Vessels in the Oil Industry. J. C. Holmberg. (Welding Journal, 1946, vol. 25, Apr., pp. 329-332). Many examples of welding on high-pressure vessels, heat exchangers, and other oil-refinery equipment are described and illustrated.

The Use of Direct Transformation Data in Determining Preheat and Postheat Requirements for Arc Welding Deep-Hardening Steels and Weld Deposits. L. F. Bowne, jun. (Welding Journal, 1946, vol. 25, Apr., pp. 234-S-241-S). It is shown how to use T.T.T. (time-temperature-transformation) curves to develop preheating and postheating schedules so as to ensure the correct ductility and hardness in the heat-affected zone of welds in deep-hardening steels.

Special Oxyacetylene Machine Cutting Applications. R. F. Helmkamp. (Welding Journal, 1946, vol. 25, Mar., pp. 213-222). Numerous types of oxy-acetylene cutting machines, many using multiple burners, and the work done with them are described and illustrated.

Stack Cutting Plates with Multiple Torch Setup. M. Keaveny. (Steel, 1946, vol. 118, Mar. 25, pp. 126-128). An account is given of the conversion to peace-time production of flame-cutting equipment originally installed for the cutting of tank armour plate. By the use of a six-torch equipment, seven thicknesses of 1/4-in. steel plate can be cut in one operation in less time and with less cost than in other methods of fabrication.

Acetylene Proves Economical in Flame-Cutting Steel. G. V. Slottman. (Machinist, 1946, vol. 90, June 1, pp. 304-305). The operating characteristics of the fuel gases (town's gas, natural gas, propane, and acetylene) when burned with oxygen in a torch and used to cut steel plates up to 4 in. in thickness were determined. The oxy-acetylene flame preheated steel faster than the flame from the other gas mixtures. Acetylene required less oxygen per unit of heat developed than any of the other gases. For equivalent cuts in steel the total oxygen consumption with acetylene was considerably less than with any other commercial fuel gas.

Flame Cutting, Flame Hardening and Welding on Railroads. J. W. Kenefic. (Welding Journal, 1946, vol. 25, Apr., pp. 299-307). How American railway companies are making extensive use of oxy-acetylene cutting machines and flame-hardening and welding techniques for maintenance and repair work, is described with many examples.

MACHINING

(Continued from p. 11 A)

On the Art of Cutting Metals. O. W. Boston. (Mechanical Engineering, 1946, vol. 68, Apr., pp. 302-304, 313). The results of investigations to discover the optimum machining conditions, in particular, F. W. Taylor's results published in 1906 after 26 years work, are reviewed. It is asserted that technical societies and government departments are carrying out too many entirely unco-ordinated investigations at the present time.

Machinability and Structure of Ferrous Materials. C. Sykes. (Institution of Mechanical Engineers, Conference on Machinability, May, 1946, pp. 1-2).

The Mechanics of the Cutting Operation. R. N. Arnold and G. A. Hankins. (Institution of Mechanical Engineers, Conference on Machinability, May, 1946, pp. 4-6).

Testing Methods Using Pendulum Machines. A. S. Kenneford. (Institution of Mechanical Engineers, Conference on Machinability, May, 1946, pp. 7-9). A pendulum-type testing machine for machinability tests is described; it measures the energy absorbed per unit volume of material removed.

Notes on Machinability Testing Apparatus and Tests Carried Out at the Naval Ordnance Inspection Department, Sheffield, Including a Development of the Drill Test. D. G. W. Curry. (Institution of Mechanical Engineers, Conference on Machinability, May, 1946, pp. 10-12).

Standardization of Tools for Machinability Tests. C. H. Booth. (Institution of Mechanical Engineers, Conference on Machinability, May, 1946, pp. 12-13).

A Tentative Method of Assessment of Machinability. C. W. George. (Institution of Mechanical Engineers, Conference on Machinability, May, 1946, pp. 14-21).

Tool Wear as a Measure of Machinability. C. Eatough. (Institution of Mechanical Engineers, Conference on Machinability, May, 1946, pp. 21-23).

The Effect of Speed, Feed, and Angle on Machinability. W. Whitworth Taylor. (Institution of Mechanical Engineers, Conference on Machinability, May, 1946, pp. 24-25).

Tool Materials. J. E. Attwood. (Institution of Mechanical Engineers, Conference on Machinability, May, 1946, pp. 26-27).

Cutting Fluids, Chipbreakers, etc. W. A. Carter. (Institution of Mechanical Engineers, Conference on Machinability, May, 1946, pp. 27-29).

Machinability in Relation to Economy of Production—Heavy Engineering. G. M. Baker. (Institution of Mechanical Engineers, Conference on Machinability, May, 1946, pp. 29-30).

Machinability in Relation to Economy of Production—Medium Engineering. L. Johnstone. (Institution

of Mechanical Engineers, Conference on Machinability, May, 1946, pp. 30-31).

Machinability in Relation to Economy of Production—Light Engineering. P. C. Redwood. (Institution of Mechanical Engineers, Conference on Machinability, May, 1946, p. 32).

Measurements of Temperatures in Metal Cutting. A. O. Schmidt, O. W. Boston, and W. W. Gilbert. (Transactions of the American Society of Mechanical Engineers, 1946, vol. 68, Jan., pp. 47-49). Measurements of the heat developed in a metal-cutting operation, as well as investigations of cutting and chip temperatures by the authors, have indicated that the chip temperature is uniform at the higher cutting speeds when all other conditions are kept constant. The temperature of the tool increases with the cutting speed, and the amount of metal removed before tool failure will generally be inversely proportional to that speed.

Tungsten Carbide Tools. (Steel, 1946, vol. 118, Mar. 25, pp. 106-108). The special characteristics of tungsten-carbide tools make some simple precautions necessary in their employment. The causes of certain troubles are listed, and instructions for the best use of these tools are given.

Experiences with Carbide-Tipped Tools. M. E. Feldstein. (Mechanical Engineering, 1946, vol. 68, Apr., pp. 307-313). A detailed description is given of the system of carbide-tipped tool design, manufacture, and maintenance established at a plant of the General Motors Corporation.

Machining Stainless Steels. J. Woolman. (Iron and Steel, 1946, vol. 19, May, pp. 179-182; Machine Shop Magazine, 1946, vol. 7, May, pp. 37-42). The results of sawing, turning, drilling, and tapping tests on various types of stainless steel are presented and discussed. It is shown that when free-cutting elements have been added to the steel its machinability is greatly improved and is practically equal to that of normalized medium-carbon steel. The broken chips produced with small drills and taps readily clear the flutes in these tools. The free-cutting stainless steels also have a much lower tendency to seize when in moving contact with metals.

Measurement of Surface Roughness. C. J. Posey. (Mechanical Engineering, 1946, vol. 68, Apr., pp. 305-306, 338). Two profiles obtained by instruments measuring surface roughness may not be geometrically similar in the Euclidean sense although they behave in a similar manner with regard to friction. Their similarity may be regarded as statistical. A method of measuring this statistical similarity is described.

CLEANING AND PICKLING OF METALS

Etching Steel with Oxalic Acid before Industrial Chromium Plating. G. R. Makepeace. (Metal Finishing, 1945, vol. 43, Sept., pp. 364-367). A detailed

description is given of the process of etching steel in oxalic acid to prepare the surface for chromium plating. It consists of an anodic treatment at room tem-

perature in a 10% solution of oxalic acid containing a wetting agent. After cleaning in an alkaline solution and rinsing in cold water the work is transferred to the oxalic acid bath. The current is switched on, using 6-8 V. with a current density of 0.5 to 1.0 amp./sq. in. For the first few seconds no gassing occurs on the work, but the attack is rapid and the work becomes covered with a green film of ferrous oxalate. Gassing then starts and quickly spreads over the entire surface, sweeping away the green film and leaving a satin-grey clean finish. After etching, the part is transferred to the chromium plating tank without rinsing. Important economic advantages are claimed for the process.

Removing Sand and Scale from Gray Iron Castings. (Iron Age, 1946, vol. 157, May 16, p. 51). The removal of sand and scale from grey iron pump castings is described. The castings are immersed in a bath of caustic soda containing a little sodium hydride and held at 700° F. They are washed twice in baths of water at room temperature and then dipped for 1 min. in dilute sulphuric acid. Finally, they are washed in a neutralizing bath.

Method of Evaluating Metal Cleaners. S. Spring, H. I. Forman, and L. F. Peale. (Industrial and Engineering Chemistry, Analytical Edition, 1946, vol. 18, Mar., pp. 201-204). A quantitative method for evaluating the performance of alkaline metal-cleaning solutions is described and discussed.

The Balanced Action Bath and Its Position in Modern Pickling Technique. P. De Lattre. (Sheet

Metal Industries, 1946, vol. 23, Apr., pp. 685-694; May, pp. 899-901). The advantages and disadvantages of pickling in sulphuric acid and in hydrochloric acid are reviewed and the theory of the "balanced action bath" is explained. This bath contains both acids, for the addition of hydrochloric acid to a ferrous sulphate solution makes it practicable to reduce very markedly its content in ferrous sulphate, producing ferrous chloride and liberating sulphuric acid. This has many advantages as it is then possible to keep the FeSO_4 content within such limits that its bad effects are nullified, besides making for a very high speed of reaction of the solution upon iron and its oxides.

Automatic Mechanical Pickler Affords from 40-60 Per Cent. Savings. J. D. Knox. (Steel, 1946, vol. 118, Apr. 29, pp. 123-124). A description is given of a pickling tank for bars and tubes in which the latter lie in a cradle of two chains. Lifting the chains on one side of the tank with a crane causes the bars to roll and thus exposes all parts of the surface to the action of the solution.

Analysis of Hydrofluoric-Nitric Acid Stainless Steel Pickling Bath. W. E. McKee and W. F. Hamilton. (Metal Finishing, 1945, vol. 43, Aug., pp. 332-333, 339). For the efficient control of hydrofluoric-nitric acid pickling baths for stainless steel rapid methods of chemical analysis are required. In this paper procedures are described for determining the total acidity, and the iron, fluoride, and nitrate contents.

COATING OF METALS

Chrome Plating of Barrels by the Heinrich Reining G.m.b.H. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXXII-64). This report consists of translations of laboratory reports taken from Heinrich Reining G.m.b.H., Enger, Westphalia, dealing with the chromium plating of machine-gun barrels 7.92 mm. inside dia., the thickness of the plating being 0.012-0.020 mm. Experiments were conducted on the plating of tubes up to 8.8 cm. in dia.

Protection against Corrosion by Chromium-Diffusion Zones. G. Becker, K. Daeves, and F. Steinberg. (Zeitschrift des Vereines deutscher Ingenieure, 1941, vol. 85, Feb. 1, pp. 127-129). Methods of impregnating the surface of steel with chromium to a depth of 0.1 mm. are reviewed. This surface layer attains a corrosion resistance equal to that of a 30%-chromium steel.

Babbitting Large Cast-Iron Bearing Shells. L. F. Train. (Iron Age, 1946, vol. 157, Apr. 4, pp. 84-85). The design and construction of equipment installed at the works of John Bertram & Sons Co., Ltd., for the tinning and babbitting of large cast-iron bearing shells are described, and the procedure is discussed.

Welsh Tinsplate Industry. J. H. Mort. (Iron and Steel, 1946, vol. 119, May 10, pp. 223-232). A review of the history of the Welsh tinsplate industry is presented from which the causes of its decline are deduced and suggestions as to remedies are made.

A Survey of the Practices of the German Can Industry during the Second World War. (Combined Intelligence Objectives Sub-Committee, File No. XXX-85, 1946).

Terne-Coated Sheet. J. H. Mort. (Iron and Steel, 1946, vol. 119, May, pp. 189-191). Methods of calculating the weights and thicknesses of lead-tin alloy coatings on steel are explained and tables of data relating to terne-coated sheets are presented.

Silicon-Impregnated Steels. H. J. Ihrig. (Iron Age, 1946, vol. 157, Apr. 4, pp. 73-78). Although high-silicon iron alloys have desirable properties, the use of these alloys has been limited, owing to difficulties in their processing. Most of these difficulties can be obviated by the adoption of silicon-impregnation methods, and the equipment, technique, and materials to be used for optimum results on a commercial scale are described.

Rustproof Coating Survives Die-Stamping. (Steel, 1946, vol. 118, May 6, p. 155). Brief particulars of the Banox process of applying an extremely thin coating to steel, zinc, and other metals are given. This is a phosphate coating sprayed on at room temperature. It acts as a rust-preventative and is sufficiently plastic to permit bending or stamping without cracking.

Organic Protective Coatings. (Combined Intelligence Objectives Sub-Committee, File No. XXXI-21,

1946 : H.M. Stationery Office). A survey is presented of German firms and personalities concerned with equipment used in the testing and manufacturing of organic protective coatings.

Corrosion-Resistant Plastic Coating. (Steel, 1946, vol. 118, Mar. 11, pp. 114, 144). A vinyl resin plastic coating was developed by an American company for protecting pickling and plating tanks and other equipment from spillage, fumes, and heat. It adheres well to steel, concrete, and wood surfaces and offers excellent resistance to alkalis, acids, oils, and greases.

Plastic Skin Protective Coatings Convert to Peace-Time Applications. B. Gould. (Corrosion and Material Protection, 1946, vol. 3, Feb., pp. 6-9, 12). The encasing of metal parts in a skin of plastic material as a protection against corrosion, a method developed during the war and now available for peace-time industry, is described. The coating, which is formed by hot-dipping, is transparent, waterproof, corrosion-proof, and abrasion-resisting. The protection can be applied in 2-5 sec., lasts indefinitely, and is completely, easily, and quickly removable when the part is required for use.

Paint Manual with Particular Reference to Federal Specifications. P. H. Walker and E. F. Hickson. (United States National Bureau of Standards, 1945, Building Materials and Structures Report BMS 105). This manual presents recommendations by the National Bureau of Standards and co-operating

organizations for the most effective use of painting materials meeting Federal Specifications. Chiefly non-technical in nature, the manual provides practical information on the application of protective coatings. Descriptions of some 60 paints and paint products are included. The causes of paint failures are traced and remedies suggested.

Infra-Red Heating. (Automobile Engineer, 1946, vol. 36, Mar., pp. 133-134). A description is given of some war-time developments in infra-red heating equipment for the rapid drying of paints on aeroplane fuel tanks and other aeroplane parts.

Metal Finishing with Infra-Red Heat. J. Parina, jun. (Steel, 1946, vol. 118, Mar. 11, pp. 95-96, 138). An illustrated description is given of the infra-red-ray heating equipment at the works of a motor-lorry body builder in Cleveland, Ohio. This consists of two tunnel-shaped ovens the sides and roofs of which are made up of banks of infra-red lamps. One tunnel is used for drying the priming coat and the other for baking the finishing coat at temperatures of 270° and 225° F. respectively.

A Physical Investigation of the Mechanism of the Drying of Paint Films. W. König. (Korrosion und Metallschutz, 1940, vol. 16, Oct., pp. 344-351). The drying of paint is due to the gradual changes of the paint from the liquid to the amorphous solid state. A method, using a pendulum-type hardness tester, which enables the drying process to be followed is described.

PROPERTIES AND TESTS

(Continued from pp. 11 A-13 A)

Metallic Materials Inspection. J. E. Garside. (Metal Treatment, 1946, Spring Issue, pp. 3-18). The author covers practically the whole range of procedure applicable to the non-destructive testing of materials, both ferrous and non-ferrous. The determination of chemical composition by physical and chemical methods is dealt with. The determination of physical condition is considered in relation to hardness and other mechanical properties, and methods are described for ascertaining metal-wall and coating thicknesses, for detecting surface defects and unsound material, and for determining structure.

Inspection and Testing of Materials—Some Recent Developments. J. W. Donaldson. (Metal Treatment, 1946, vol. 13, Spring Issue, pp. 61-69). A review of fairly recent work in the United States on the value of various methods of testing, mainly non-destructive methods, is made.

The Identification of Mixed Alloy Steels by Practical Methods. W. A. Ledsam. (Australian Institute of Metals : Australasian Engineer, 1946, Mar. 7, pp. 72-74). Rapid methods of identifying alloy steels are described. Of these, one of the most useful is the spark test, and, in conjunction with it, the pellet test. In the latter, the burnt particles from the spark test are collected on a sheet of paper and examined at 25-30 diameters; when chromium is present the pellets are spherical with a matt grey

surface; molybdenum causes the pellets to become hemispherical, and hollow if the carbon is high; vanadium causes the pellets to erupt like a miniature volcano and it produces a black surface on them.

The Identification and Recovery of Scrap Metal. (Machinery, 1946, vol. 68, May 23, pp. 659-663). Rapid chemical spot tests for identifying the metals present in ferrous and non-ferrous scrap metals are described and recommendations are made on the cleaning, storage, and refining of turnings, borings, and other forms of scrap.

Ferrous Physical Metallurgy. Long-Range Fundamental Research Lags in U.S. While Soviet Russia Bids for Lead. J. H. Holloman. (Mining and Metallurgy, 1946, vol. 27, Feb., pp. 89-93). Research in the field of physical metallurgy in the U.S.A., Russia, Germany, and England is reviewed, and the positions of research in these countries at the closing period of the second World War are compared. The opinion is expressed that of the great nations of the world Russia alone has maintained the long-range view and has continued to foster research of the most fundamental type. Suggestions for the organization of future research are made.

Essential and Fundamental Characteristics of the Strength Properties of a Material. C. Benedicks. (Metal Treatment, 1946, vol. 13, Spring Issue, pp. 53-59). An abridged English translation is presented

of a paper which appeared in *Jernkontorets Annaler*, 1945, vol. 129, No. 9, pp. 557-570 (*see* Journ. I. and S.I., 1945, No. II., p. 167 A).

Chemical and Metallurgical Control Machine Tool Manufacture. D. G. P. Paterson. (*Sheet Metal Industries*, 1946, vol. 23, May, pp. 925-932). An account is given of the chemical and physical methods of testing employed by a Coventry firm of machine-tool manufacturers for the strict and carefully planned technical control of materials and processes.

The Mechanism of the Tensile Test. E. Siebel. (*Wissenschaftliche Abhandlungen der deutschen Materialprüfungsanstalten*, 1944, No. 5, pp. 1-4). The plastic behaviour of the material in the necking zone of tensile-test specimens was studied and a method of calculating the stress distribution in this zone is explained. The discussion of the experimental results indicates that the region of material flow becomes shorter with increasing necking.

The Determination of Proof Stress without an Extensometer. J. G. H. Brown. (*Metallurgia*, 1946, vol. 33, Apr., pp. 301-302). A description is given of a method of determining the proof stress of a metal, using a small specimen with a gauge length of only 1 in., without the aid of an extensometer.

A Mechanical-Optical Extensometer for Static Measurements. H. Freise. (*Zeitschrift des Vereines deutscher Ingenieure*, 1941, vol. 85, Nov. 29, pp. 919-920). A detailed description is given of a rotating-mirror extensometer of improved design and high accuracy.

Stress Analysis Methods—Choice Determined by Part's Design and Application. W. M. Murray. (*Meehanite Research Institute: Materials and Methods*, 1946, vol. 23, Apr., pp. 1002-1006). Photo-elastic, strain-gauge, and stress-coat (or brittle lacquer) methods of determining the distribution of stress in metal parts are described so as to show the type of problem to which each is applicable.

Stress Measurement by Photo-Elastic Methods. W. J. Kearton. (*Transactions of the Liverpool Engineering Society*, 1945, vol. 66, pp. 129-146). A brief explanation of the photo-elastic method of stress measurement and an account of some results obtained by it are given.

Electric Strain Gages Aid Machine Design. V. E. Hillman. (*Iron Age*, 1946, vol. 157, Apr. 11, pp. 50-53). As a means of revealing hidden weaknesses, or conversely, of indicating areas of excessive strength with resultant overweight, the electric strain gauge is proving an invaluable tool in the hands of structural and machine designers. The principle of operation and method of using these gauges, and the indicating equipment necessary for observing the results, are described.

Ball Wear and Functioning of the Ball Load in a Fine-Grinding Ball Mill. W. I. Garms and J. L. Stevens. (*American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1984: Mining Technology*, 1946, vol. 10, Mar.). Particulars and results are given of tests upon the influence of the ball load and the characteristics of ball wear at a plant using cylindrical drum mills with trunnion feed and discharge.

Fatigue Tests on Wires and Wire Ropes. W. Heilmann. (*Wissenschaftliche Abhandlungen der deutschen Materialprüfungsanstalten*, 1939, No. 3, pp. 27-30). Methods of investigating the bending-fatigue strength of single wires and of wire ropes are discussed.

Evidence of the Fatigue of Metals Subjected to Alternating Stresses by the Determination of the Surface Stress with X-Rays. R. Glocker, W. Lutz, and O. Schaaber. (*Zeitschrift des Vereines deutscher Ingenieure*, 1941, vol. 85, Oct. 4, pp. 793-800). When determining the surface stresses in metal by X-rays the elastic elongation of the crystallites is measured and the elastic stress is calculated directly from this. In this paper an apparatus and X-ray technique are described in which, during the torsional fatigue testing of steel specimens only a fraction of the stresses in the surface layer is absorbed elastically. If this fraction, as measured by the X-ray technique described, decreases during the test, it indicates a decrease in the strength of the specimen, and *vice versa*. This technique enables the end-point of the first of the two states of fatigue to be clearly determined, the two states of fatigue being that up to the occurrence of the first crack, and that from the first crack until fracture. The drop in fatigue strength can in fact be detected before any crack is large enough to be revealed by the magnetic-powder method.

The Torsional Fatigue Strength of High-Tensile Steel Crankshafts. H. Cornelius and F. Bollenrath. (*Zeitschrift des Vereines deutscher Ingenieure*, 1942, vol. 86, Feb. 21, pp. 103-108). An investigation of the torsional fatigue strength of low-alloy heat-treated steels is described. It was found that, with unnotched specimens 30 mm. in dia., there was a drop in the fatigue strength when the tensile strength exceeded 130 kg./sq. mm. and that this was due to the notch effect of the minute lines in the surface left by the machining operations. With some specimens drilled through the centre, on the other hand, the fatigue life continued to increase with increasing tensile strength right up to the highest-strength material tested; in such cases the notch effect of machining marks attains a value equal to that of the drilled hole only when the material is of the very highest tensile strength. The finished surface of high-tensile steel crankshafts must therefore be of the finest quality.

Time Resistance and Fatigue Strength and How They Are Affected by a Single Heavy Overloading. A. Thum and A. Esker. (*Zeitschrift des Vereines deutscher Ingenieure*, 1942, vol. 86, Mar. 21, pp. 171-174). The effect of single heavy overloads on the life and strength of steel components was studied by means of fatigue and tensile tests on butt-welded and fillet-welded plates of high-tensile steel. When the notch effect is slight (as in a butt weld) up to about 15,000 load cycles, and when it is marked (as in a fillet weld) up to about 5000 load cycles are permissible before any allowance need be made in design for differences between static and dynamic stresses. A single overload does not become dangerous to a component not subjected to notch effects until there

is visible damage such as the appearance of a crack.

The Breadth of the Scatter in the Brinell-Hardness Testing of Cast Iron and Steel. F. Roll and W. Eger. (*Zeitschrift des Vereines deutscher Ingenieure*, 1942, vol. 86, Sept. 5, pp. 545-549). The scatter of hardness-test results has frequently been studied, but the number of different testing stations taking part is usually too few to obtain a fair average of the influence of factors affecting the tests. The present report covers the data obtained from 64 laboratories representing producers and users of cast iron and steel, as well as the makers of Brinell instruments. The results are given in frequency curves and these indicate that greater latitude is required in acceptance specifications for cast iron.

The Temper-Brittleness of Steels Containing Chromium, Molybdenum and Tungsten. G. Vidal. (*Revue de Métallurgie, Mémoires*, 1945, vol. 42, May, pp. 149-155). Investigations on the susceptibility of molybdenum and tungsten steels to temper-brittleness, and on the mechanism of temper-brittleness are described. The above steels are just as susceptible to the phenomenon as chromium and manganese steels. Impact-strength/tempering-temperature and impact-strength/tempering-time curves were plotted for the different steels. The latter curves for the 1.38%-chromium steel and the 2.1%-molybdenum steel are very similar. The embrittlement takes place in the first few minutes of the tempering treatment. The temperature of testing has a marked effect on the impact strength so that temper-brittleness should not be studied by impact tests at constant temperature. There is a striking analogy between the phenomenon of temper-brittleness and the hardening effect following the heating of supersaturated solid solutions.

Magnetic-Particle Testing Prevents Railroad Failures. L. B. Sagle. (*Machinist*, 1946, vol. 90, May 25, pp. 240-241). A description is given of the magnetic-particle method of testing as used by one of the American railway companies for detecting faults in forgings.

The Supersonic Flaw Detector and Its Application in the Sheet Metal Industries. A. C. Rankin. (*Sheet Metal Industries*, 1946, vol. 23, May, pp. 893-898, 901). The supersonic flaw detector has already been described (*see Journ. I. and S.I.*, 1946, No. I., p. 68 A); in this paper its applications to problems encountered in the sheet metal industries are discussed.

Magnetic Inspection Procedure. E. D. Wilcox. (*Machinery*, 1946, vol. 68, Apr. 18, pp. 489-495). The principles of magnetic inspection as a means of discovering defects in the structure of materials are explained and the procedure described. The machines employed are generally of the rectified alternating-current or the storage-battery type, and two methods of magnetizing are used, namely, "circular" and "longitudinal," the method chosen depending upon the type of defect expected. A magnetic field is built up in and around the part under inspection and, if a crack or discontinuity be present, north poles will be formed on one edge and south poles on the other, so setting up lines of force; on the intro-

duction of a magnetic substance, *e.g.*, iron filings or iron oxide, the discontinuity will be outlined. Two other methods, *viz.*, "residual" and "continuous," are also described. The care of the apparatus, methods of demagnetization, and the type of defects located are discussed.

Investigations on Sheets of Iron and Nickel Produced Electrolytically in Layers. K. Heck. (*Wissenschaftliche Veröffentlichungen aus den Siemens-Werken*, 1941, vol. 20, No. 1, pp. 104-134). Iron-nickel sheets were produced by the electrolytic deposition of the two metals in alternate layers each about 0.003 mm. thick, and their electrical and magnetic properties were investigated. By annealing for a short time (about 20 min.) at 1000° C. a homogeneous alloy is obtained, which has useful magnetic properties.

Permanent Magnets of Iron-Nickel-Cobalt-Aluminum-Copper(-Titanium) Alloys with Preferred Magnetic Orientation. W. Zumbusch. (*Iron and Steel Institute*, 1946, Translation Series No. 272). This is an English translation of a paper which was published in *Archiv für das Eisenhüttenwesen*, 1942, vol. 16, Sept., pp. 101-112. (*See Journ. I. and S.I.*, 1946, No. I., p. 13 A).

Modern Permanent-Magnet Materials. H. Nathorst. (*Iron and Steel Institute*, 1946, Translation Series No. 273). This is an English translation of a paper which was published in *Jernkontorets Annaler*, 1942, vol. 126, No. 10, pp. 471-525. (*See Journ. I. and S.I.*, 1943, No. I., p. 215 A).

Report on Cobaltine Alni-Steel Magnets, Robert Bosch Dispersal Plant at Engingen, Germany. (Combined Intelligence Sub-Committee, 1945, File No. XXXI-4).

Permanent Magnet Steels. W. E. Ruder. (*Iron Age*, 1946, vol. 157, May 9, pp. 65-69). The properties of permanent-magnet alloy steels are reviewed.

High Temperature Engineering. J. Taylor. (*Iron and Steel*, 1946, vol. 19, May, pp. 217-220). Methods of testing the properties of steel at high temperatures are described and their merits compared. The danger of extrapolating data is stressed.

Heat-Resisting and Corrosion-Resisting Alloy Steels. F. Krupp A.G., Essen. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXXI-44). A brief report on the development and properties of heat-resisting and corrosion-resisting alloy steels by F. Krupp A.G., Essen, is presented. Particulars are given of the steels "Tinidur," "Cromadur," and "Vanidur."

Report on Visit to Germany and Austria to Investigate Alloys for Use at High Temperature. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 396: H.M. Stationery Office). This report contains information on the heat-resisting steels developed in Germany and Austria since 1937 with particular reference to the requirements of gas turbines.

Properties and Characteristics of 27% Chromium Iron. H. D. Newell. (*Metal Progress*, 1946, vol. 49, May, pp. 977-991, 994-1004). A comprehensive account is given of the properties of a heat-resisting steel containing 27% of chromium and 0.25% max.

of carbon. Its embrittlement characteristics and resistance to corrosion when used in plant for the dehydrogenation of butane are specially considered.

Ni Span. W. A. Mudge and A. M. Talbot. (Iron Age, 1946, vol. 157, Apr. 25, pp. 66-70). Data on the properties of three recently developed iron-nickel-titanium alloys of the Invar and Elinvar types possessing low thermal expansion, high thermal expansion, and constant modulus of elasticity over a definite range of temperature, respectively, are presented and discussed. The materials are known commercially as the Ni-Span alloys.

Heat-Resisting Cr-Mn Steels as Substitutes for Cr-Ni Steels. M. Schmidt and W. Lamarche. (Korrosion und Metallschutz, 1940, vol. 16, Dec., pp. 425-427). The properties of chromium-manganese steels are compared with those of chromium-nickel steels, and it is shown that the former can be used in place of the latter where heat-resistance at up to 950° C. is required. The former are, however, sensitive to carburizing gases and should therefore not be used in reducing atmospheres.

The Creep of Heat-Resisting Steels in the Temperature Range of 800° to 1200° C. G. Hahn. (Wissenschaftliche Abhandlungen der deutschen Materialprüfungsanstalten, 1944, No. 5, pp. 13-17). Creep tests on six heat-resisting steels are described in which were determined the stresses which would produce permanent elongations of 0.2%, 0.5%, and 1% in 1000 hr. at temperatures in the 800-1200° C. range. Four steels contained up to 1.03% of nickel with 6.10%, 8.70%, 16.20%, and 23.10% of chromium respectively, the fifth was a 9/4.5/1 chromium-aluminum-titanium steel, and the sixth was a 23/18 chromium-nickel steel. The testing apparatus and procedure are described and the results are shown by graphs.

The Solubility of Hydrogen in Molten Iron-Silicon Alloys. H. Liang, M. B. Bever, and C. A. Floe. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1975: Metals Technology, 1946, vol. 13, Feb.). The solubility of hydrogen in representative compositions of the iron-silicon system containing up to about 65 wt.-% of silicon is studied as a function of temperature and composition, and conclusions are given.

The Behavior of Hydrogen in Steel during Pickling. C. A. Zapffe. (Wire and Wire Products, 1946, vol. 21, Feb., pp. 149-157). Preparatory to a study of the deleterious effects of hydrogen in wire and other steel products during pickling, the behaviour and effects of hydrogen in steels in general, and especially the part played by hydrogen in the formation of blisters and voids, are widely reviewed and illustrated. In wire products the principal trouble due to hydrogen is embrittlement, and this results from the entrapping of hydrogen gas under high pressure within the microscopic voids which traverse the interior of each grain. Some of the hydrogen evolved during pickling enters the steel by passing right into the grain, and not by passing through the grain boundaries as has previously been stated. The influence of hydrogen embrittlement upon cracking and corrosion is also considered.

The Problem of the Hydrogen Embrittlement of Steel in Galvanic Processes. H. Fischer and H. Bärman. (Korrosion und Metallschutz, 1940, vol. 16, Dec., pp. 405-417). The manner in which the composition of plating baths and the plating conditions affect the hydrogen embrittlement of steel was investigated. The embrittlement was measured by the number of reversals before fracture of specimens 24 mm. wide \times 0.35 mm. thick in a 180°-bend test. In alkaline cyanide baths the embrittlement was equally great with electrolytes containing zinc, cadmium, copper, brass, or silver. The embrittlement occurred in the first minute of deposition; after that the coating hindered the penetration of hydrogen. Increasing the cyanide content promoted embrittlement. Increasing the current density increased the rate of deposition in the first minute and reduced the embrittlement. Raising the temperature of the bath increased the embrittlement. Small additions of zinc to caustic soda reduced the number of bends to fracture very considerably with cathodic deposition, but in the presence of cyanides, zinc no longer had this effect. With weak acid electrolytes for depositing zinc, nickel, or lead there was very slight, almost negligible embrittlement. It is possible in most cases to select an electrolyte for a material sensitive to embrittlement which will not reduce the number of bends to fracture at all or only reduce the number very slightly.

Tailoring 18-8. W. G. Hubbell. (Steel, 1946, vol. 118, May 13, pp. 112, 136-140). The relative merits of different stainless steels in regard to their welding, pressing, and other fabricating properties are discussed. The results of many tests indicated that: (1) The amount of free ferrite is inversely proportional to the nickel content; (2) the forming properties improve with decreasing amounts of ferrite; (3) increasing the nickel content from 8% to 11-12% improves the forming properties; and (4) columbium-stabilized stainless steel has better welding properties than that stabilized with titanium.

Effect of Alloying Elements on Mechanical Properties. M. Gensamer. (American Society for Metals, Campbell Memorial Lecture: Iron Age, 1946, vol. 157, Feb. 14, pp. 66-71). **Strength and Ductility.** M. Gensamer. (Metal Progress, 1946, vol. 49, Apr., pp. 731-734). The problem of how alloying elements in solid solution and undissolved compounds distributed in solid solutions affect, quantitatively, the mechanical properties of steel is discussed and methods of expressing and interpreting the results of tensile tests are considered. Generally speaking, the strength is not sensitive to local variations in composition and structure, but in solid solutions it is dependent on the composition. Ductility, on the other hand, is very greatly affected by local conditions. Local ductility, unless very low, has little effect on energy absorption in a structure; the distribution of deformation is apt to be of more consequence.

Ferrous Physical Metallurgy. Progress Reported in Studies of Hardenability, Graphitization, Embrittlement, and Dilatometry. F. W. Walters, jun. (Mining and Metallurgy, 1945, vol. 26, Feb., pp. 87-89). In

spite of war-time difficulties, definite progress was made during 1944 in the understanding of the behaviour of steel and of the effect of alloying elements. Highly practical problems under study are the graphitization of low-carbon steel and weld-cracking, while investigations of more theoretical interest have concerned hardenability, isothermal reactions, the effect of hydrogen, and the interpretation of the notched-bar impact test.

Copper as an Alloy in Iron and Steel. G. K. Manning and P. C. Rosenthal. (Mining and Metallurgy, 1945, vol. 26, Dec., pp. 601-605). The use of copper as an intentionally added element in steel and cast iron is discussed, and its effects reviewed. The superior corrosion resistance and physical properties of copper-bearing steels are described.

Some Characteristics of Vanadium-Bearing Intermediate Manganese Cast Steels. G. P. Contractor and J. S. Vatchagandhy. (Journal of Scientific and Industrial Research, 1945, vol. 4, Sept., Reprint). An investigation of the properties of low- and medium-carbon intermediate-manganese cast steels with and without the addition of vanadium is described. Test results indicated that with vanadium there is a slight but distinct improvement in ductility and a decided improvement in the impact and yield strengths whilst the tensile strength is more or less unaffected.

The Effect of Titanium on the Creep Strength of Steel. P. Bardenheuer and W. A. Fischer. (Iron and Steel Institute, 1946, Translation Series, No. 277). This is an English translation of a paper which appeared in Archiv für das Eisenhüttenwesen, 1942, vol. 16, July, pp. 31-38. See Journ. I. and S.I., 1946, No. I., p. 13 A.

The Effect of Titanium on the Creep Strength of Steels. E. Houdremont and G. Bandel. (Iron and Steel Institute, 1946, Translation Series, No. 278). This is an English translation of a paper which appeared in Archiv für das Eisenhüttenwesen, 1942, vol. 16, Sept., pp. 85-97. See Journ. I. and S.I., 1946, No. I., p. 13 A.

On the Strength and Ductility of Quenched and Tempered Steel. J. B. Friedman and T. A. Volodina. (Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS, 1945, vol. 48, No. 8, pp. 559-562). Data on the mechanical properties of Chromansil steel (containing about 1% each of chromium and silicon) are presented and discussed and it is shown that whilst it behaves in a brittle manner in the tensile test after quenching and tempering, it has appreciable ductility when tested in torsion.

Tool Steels Classified. H. J. Wright. (Canadian Metals and Metallurgical Industries, Feb., 1946,

pp. 20-23, 28). Tool steels are classified into three sections, and each section is divided into three groups, the characteristics, type, analysis, and heat-treatment of which are shown on a comprehensive chart. Each section and group is described in detail, and a reference chart of all the tool steels sold in Canada is provided.

A Metallurgical Study of German Aircraft Engine and Airframe Parts. Section I. Description of Engines and Aircraft Examined. Section II. Crankshafts. Section III. Connecting Rods. Section IV. Gudgeon Pins and Wrist Pins. Section V. Cylinders and Cylinder Liners. Section VI. Inlet and Exhaust Valves. Section VII. Valve Springs. Section VIII. Gears. Section IX. Bearings. Section X. Camshafts. Section XI. Cast Components. Section XII. Miscellaneous Engine Parts. Section XIII. Airframe Components. Section XIV. Miscellaneous Parts. (Metallurgia, 1945, vol. 32, Sept., pp. 203-211; Oct., pp. 263-270; vol. 33, Nov., pp. 25-31; Dec., pp. 65-72; 1946, Jan., pp. 125-133; Feb., pp. 213-218; Mar., pp. 253-260). This report constitutes a summary of data resulting from the metallurgical examination of German aircraft engine and airframe parts by the Aero-Components Subcommittee of the Technical Advisory Committee of the Special Alloy Steel Committee formed for that purpose.

Steel Moulds for Plastics. (British Engineering Export Journal, 1946, vol. 28, May, pp. 929-931). Nickel-chromium steels and high-carbon high-chromium steels for making moulds for plastics are discussed and some specifications, with the necessary heat-treatment, are given.

Cylinder Liners. (Automobile Engineer, 1946, vol. 36, Apr., pp. 149-155). A description is given of the alloys and processes developed by a Birmingham firm for making wear- and heat-resisting liners for internal combustion engine cylinders. Two special cast irons have been developed, namely, Silmocrom (containing silicon 2.50-3.50%, chromium 0.60-1.50%, and molybdenum up to 0.50%) and an austenitic cast iron (containing silicon 2%, manganese 1%, nickel 13-15%, copper 5-7%, and chromium 1.5-4.0%). The centrifugal casting, machining, microstructure, inspection, and fitting of the liners are described.

The Further Development of High-Tensile Structural Steels Similar to Steel St 52. A. Fry and L. Kirschfeld. (Zeitschrift des Vereines deutscher Ingenieure, 1941, vol. 85, June 7, pp. 511-516). Details are given of the development in Germany of an ageing-resistant high-tensile structural steel with carbon up to 0.20% and manganese up to 1.6% with good welding properties.

METALLOGRAPHY AND CONSTITUTION

(Continued from p. 13 A)

Obtaining Pictures of Finely-Machined Surfaces with the Electron Microscope. B. von Borries and S. Janzen. (Zeitschrift des Vereines deutscher Ingenieure, 1941, vol. 85, Mar. 1, pp. 207-211). The

principles of the electron microscope are explained and its application to study the roughness of metal surfaces after various machining processes is described.

The Development of the Electron Microscope with Electrostatic Lenses. E. Brüche. (*Zeitschrift des Vereines deutscher Ingenieure*, 1941, vol. 85, Mar. 8, pp. 221-228). The designs and advantages of electron microscopes with magnetic and electrostatic lenses are compared and discussed. The construction of the latter is described in detail and examples of its application are given.

"Shadow-Cast" Replicas for Use in the Electron Microscope. H. Thielsch. (*American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1977: Metals Technology*, 1946, vol. 13, Feb.). The "shadow-casting" replica technique for the examination of metallurgical specimens in the electron microscope is discussed, and a new "shadow-casting" process is described by means of which replicas of high contrast and sharpness are produced with short preparation time.

Microscopical Examination of Metals and Alloys, with Special Reference to Electrolytic Etching and Photomicrography in Colour. K. J. B. Wolfe. (*Metal Treatment*, 1946, vol. 13, Spring Issue, pp. 25-40). It is shown that electrolytic etching has proved to be of great value to the metallurgist in obtaining consistently good micrographs from metals and alloys that are difficult to etch by normal chemical means; these include aluminium, copper, and nickel-base alloys. The reagent produced for nickel-base alloys has also been found satisfactory for austenitic chromium-nickel steels. An electrolytic etching outfit suitable for quick and accurate work is described, and typical photomicrographs obtained with it are shown. Methods are also given for the production of transparencies suitable for lantern slides, and for producing photomicrographs in natural colours.

A Universal Metallographic Polishing Procedure. W. C. Coons. (*Metal Progress*, 1946, vol. 49, May, pp. 956-959). A simple procedure for polishing metallographic specimens is described. The materials used consist of three cloths (canvas, silk, and "Gamal"), an abrasive suspension of 1 part of 600-mesh carborundum in 10 parts of distilled water for use on the canvas, and a polishing abrasive called "C-RO" for use on the silk and "Gamal" cloths. Micrographs of iron, steel, and alloys of aluminium, copper, and magnesium are shown in support of the claim that the procedure is applicable to both ferrous and non-ferrous metals.

Radiographic and Fluoroscopic Interpretation of Casting Irregularities. T. E. Piper. (*Iron Age*, 1946, vol. 157, May 2, pp. 46-49). The use of X-rays and the fluoroscope for the non-destructive testing of castings for aeroplanes is described and the definitions obtained by the two methods are compared. The appearance of 14 types of defect as indicated by X-rays is illustrated.

Inspection of Steel Castings. C. F. Rohlkoetter. (*American Foundryman*, 1946, vol. 9, Feb., pp. 70-74). Procedure and methods for the inspection of steel castings are reviewed, and X-ray, radiographic, laboratory, impact, and hardness testing are discussed. The use of quality control charts is found to be helpful.

Inspection of Heavy Steel Sections with 1000-Kilovolt

X-ray Unit. (Steel, 1946, vol. 118, Mar. 25, pp. 122-124). A 1000-kV. X-ray unit, recently installed at the Bethlehem plant of the Bethlehem Steel Company and designed for the routine inspection of heavy steel sections up to 8 in. thick, is described. The unit affords rapid inspection of castings with ease of manipulation and safety.

Industrial Applications of X-Ray Stress Analysis. D. M. McCutcheon. (*Industrial Radiography*, 1946, vol. 4, Spring Issue, pp. 9-16). A qualitative analysis of surface stresses in metals can be made by a number of fairly simple X-ray diffraction methods. The difficulties in applying these methods to heat-treated steels are discussed. Development of the Geiger counter offers considerable promise in speeding up the process.

Metallurgical Aspects of X-Ray Tube Manufacture. M. J. Zunick. (*Iron Age*, 1946, vol. 157, Apr. 11, pp. 56-59). Some of the unusual operations involved in X-ray tube manufacture, including casting of the anodes, mounting of the filament, preparation of targets, glass-to-metal sealing, and tube exhausting, are discussed from the viewpoint of the metallurgist. Some notes on the preferential heating characteristics of vacuum furnaces are included.

The Structure of Heat-Resistant Austenitic Steel. I. The Kinetics of Grain Growth and the Solution of Carbides in EI-69 Steel upon Heating. G. V. Akimov and Z. L. Minz. (*Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS*, 1945, vol. 48, No. 3, pp. 185-186). The reasons for the pronounced decrease in plasticity when the hardening temperature of austenitic 13/13/2 chromium-nickel-tungsten heat-resisting steel is increased from 1050-1100° C. to 1200-1250° C. were investigated. With short periods of heating at 900° C. the coagulation of microscopically invisible carbides predominates; at other temperatures the solution and coagulation of microscopically detectible carbides predominate. With very long periods of heating (e.g., 50 hr.) the carbides coagulate into extremely large particles 20 to 100 times coarser than the original carbides in the steel.

Structure of Austenitic Heat-Resistant Steel II. Processes Involved in the Ageing of Hardened EI-69 Steel. G. V. Akimov and Z. L. Minz. (*Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS*, 1945, vol. 48, No. 8, pp. 565-566). A comparison was made of the structures formed during the ageing at temperatures in the 700-850° C. range of specimens of steel EI-69 which had been hardened at 1050° C. and 1250° C. This is the same steel as that referred to in the preceding abstract. During the ageing of fine-grained steel hardened at the lower temperature the carbides are deposited evenly throughout the whole grain. These carbides are rounded and about the same size as those which remained undissolved when the steel was heated before hardening. In the specimens tempered at 1250° C. the carbides are precipitated in a very finely dispersed form which have a high thermal stability.

The Structure of Tempered Martensite. W. J. Wrażej. (*Iron and Steel Institute*, 1946, this Journal, Section I). Martensite must be regarded as a solid solution of carbon in α -iron. The 002, 112, and

202 lines on X-ray photographs taken of 0.9% and 1.2% carbon steels distinctly show its tetragonal structure. In a steel of eutectoid composition the ratio of carbon atoms to iron atoms is 1:24, *i.e.*, in martensite of such a composition, one carbon atom belongs to a set of twelve α -iron unit cells, thus causing tetragonal distortion. X-ray examination of quenched samples tempered at 100° C. for 24 hr. showed that martensite changes on tempering into ferrite and cementite, the latter being precipitated as particles of primary size (multiples of a unit cell) and shape (plates). The tempered material has thus not the structure ascribed to β -martensite, *viz.*, cubic martensite holding cementite in solution. Owing to the difference between the ferrite and cementite phases in both structure and parameter there will be internal stresses in tempered martensite. These, together with the small particle size, cause the broadening of the lines on the X-ray photographs, as evidenced by calculations. Martensite can be tempered even at a temperature as low as 100° C., the first stage of troostite being formed.

Temperature Range of Martensite Formation. R. A. Grange and H. M. Stewart. (Steel, 1946, vol. 118, May 13, pp. 126-130). A study was made of the formation of martensite in fourteen carbon and low-alloy steels. The amounts of martensite formed on quenching in molten metal baths and subsequently in brine were determined by an etching method, the temperatures of the first quench being lowered by stages through the range of martensite formation. Equal increments of martensite were not formed on cooling through successively lower equal temperature intervals. A greater temperature change was required to form the first 10% of martensite than to form the second 10%. The effects of silicon, manganese, nickel, chromium, and molybdenum on the martensite-formation point are pointed out, and a formula for estimating this point from the chemical composition is developed.

The Neutralization of Sulphur in Cast Iron by

Various Alloying Elements. H. Morrogh. (Iron and Steel Institute, 1946, this Journal, Section I). A metallographic examination has been made of the sulphide phases in irons of low manganese and high sulphur contents to which varying amounts of nickel, molybdenum, copper, chromium, and aluminium have been added. In the absence of these elements, manganese and iron sulphides would have been present. Nickel in amounts up to 20% gave no new sulphides; molybdenum did not influence the form of the sulphides until 2% of the element had been added. In the presence of low manganese contents complex copper-sulphide/iron-sulphide/manganese-sulphide aggregates were obtained. Complex sulphides were found in all irons with chromium contents of between 1 and 30%; 2-7% of aluminium caused the sulphides to be present as aluminium (manganese) sulphide. With sufficient manganese to balance normal sulphur contents, manganese sulphide was the only sulphide phase to be seen except in the case of high chromium contents.

Abnormal graphite structures were obtained in some of the irons containing nickel or copper. It is suggested that these are formed by the solidification of the iron in the white condition, followed by carbide breakdown after solidification. This process may be caused by the effect of temperature upon the reaction between manganese and iron sulphide.

Constitution of Commercial Low-Carbon Iron-Silicon Alloys. R. L. Rickett and N. C. Fick. (American Institute of Mining and Metallurgical Engineers, Technical Publication, No. 1966: Metals Technology, 1946, vol. 13, Feb.). An investigation of the constitution of a series of commercial silicon steels containing 0.05-0.08% of carbon and 0.20-4.1% of silicon, over the temperature range 1300-2500° F. is described. Conclusions regarding the A_1 temperature and the influence of chemical composition and temperature on the formation of austenite and ferrite are given.

CORROSION OF IRON AND STEEL

Cast Iron in the Chemical Industries. F. L. LaQue. (Metal Treatment, 1946, vol. 13, Spring Issue, pp. 21-24). The corrosion-resisting properties of grey cast iron and alloy cast irons are reviewed.

Corrosion of Steels. (Corrosion and Material Protection, 1946, vol. 3, Mar., pp. 9-12). The corrosion resistance of copper-bearing steels, irons, plain carbon steels, low-alloy high-strength steels, and carbon steels, and the influence of various atmospheres and constituents upon corrosion are discussed and compared in a statement prepared by the United States Steel Corporation of Delaware. Tests in seawater, and the application of protective non-metallic coatings, are also referred to.

Reminiscences of Early Corrosion Research. F. N. Speller. (Corrosion and Material Protection, 1946, vol. 3, Mar., pp. 6-8, 26). The development of corrosion research is discussed, and some investigators

mentioned. Important developments up to 1930 are tabulated.

Recent Work on Corrosion and Oxidation. U. R. Evans. (Journal of the Chemical Society, 1946, Mar., pp. 207-214). The results of recent investigations on corrosion and oxidation are reviewed, the reactions being classified as either film-forming or non-filming.

The Present State of Our Knowledge of Rusting and the Corrosion-Passivation of Iron on the Basis of Research Since the Turn of the Century. W. J. Müller. (Korrosion und Metallschutz, 1940, vol. 16, Nov., pp. 365-396). A very comprehensive review of corrosion research is presented; in it the very varied phenomena connected with rust formation are qualitatively, and to some extent quantitatively, explained by the local-current theory and the theory of metal potentials.

Corrosion of Metals and Alloys. S. J. Kennett. (Transactions of the Liverpool Engineering Society, 1945, vol. 66, pp. 16-29). The mechanism of the corrosion of metals and alloys exposed to gases, liquids, and vapours is briefly considered with examples.

Advanced Metal Preservation Methods. I. R. Such. (Steel, 1946, vol. 118, Apr. 29, pp. 90-92, 133-134). A description is given of the methods employed by the United States Navy for preventing the corrosion of the metal surfaces of layed-up ships. They include paint-spraying and applying coats or skins of plastic materials. Experiments with antifouling paint containing DDT indicate that it prevents fouling by barnacles but is not effective against marine vegetable growth.

Control of Galvanic Corrosion of Iron. C. K. Donoho and J. T. MacKenzie. (Corrosion, 1946, vol. 2, Mar., pp. 20-24). When a distinct potential difference exists between two parts of a metallic structure in a conducting medium, the more cathodic part is protected from corrosion, but at the expense of the more anodic element. Iron can be made relatively more cathodic by alloying with more noble elements which form simple solid solutions with the iron; two elements commonly used are nickel and copper. Examples are cited in which malleable iron for bolts was alloyed with 1% of copper to make them cathodic to the condenser coils in which they were used; this measure resulted in greatly decreased corrosion of the bolts.

Corrosion Problems in the Petroleum Production and Pipe Line Industry. W. F. Rogers. (Corrosion, 1946, vol. 2, Mar., pp. 59-63). The corrosion of pipelines in the petroleum industry is discussed and the methods by which some problems have been overcome are cited. With effluent waters carrying less than 1500 parts per thousand of solids and at pH values above 8.0 the addition of 2% of either sodium nitrite or sodium chromate gives almost complete protection.

Control of Pipe-Line Corrosion.—A Manual. O. C. Mudd. (Corrosion, 1945, vol. 1, Dec. pp. 192-218; 1946, vol. 2, Mar., pp. 25-58). Explanations of electrolytic, galvanic, and biochemical corrosion are offered. Methods of detecting areas of corrosion in buried steel pipe lines by instruments without excavation of the pipe are described. Finally the value of protective measures such as a combination of electrically-resistant coatings and counter-current installations and the nature of the latter are carefully examined.

Anaerobic Corrosion of Steel Pipe Due to Nitrate. D. H. Caldwell and J. B. Ackerman. (Journal of the American Water Works Association, 1946, vol. 38, Jan., pp. 61-64). The mechanism of the anaerobic corrosion of steel pipes in the presence of nitrate ions is outlined. The history of a particular case involving a water with no dissolved oxygen, having a pH value of 6.4 and containing 4-7 p.p.m. of nitrate is described. The corrosion reaction released 9.0 p.p.m. of ferrous iron. Raising the pH value to 8.0 completely arrested the corrosion both in the presence and absence of chlorination.

The Control of Fouling Organisms in Fresh- and

Salt-Water Circuits. J. G. Dobson. (Transactions of the American Society of Mechanical Engineers, 1946, vol. 68, Apr., pp. 247-260). The difficulties encountered by industrial water users due to fouling organisms are discussed. The life cycle of typical molluscs, polyzoa, sponges, barnacles, and tunicates are considered and methods of controlling them by heat, changes in salinity and oxygen content, increasing the velocity of the circulated water, acids, anti-fouling paints, screening, and poisoning are considered. Factors to be considered when designing water systems that may foul are also outlined.

Resistance of Nickel-Containing Alloys to Corrosives Encountered in the Petroleum Refineries. B. B. Morton. (Transactions of the American Society of Mechanical Engineers, 1946, vol. 68, Apr., pp. 229-235). The corrosive liquids and gases which are encountered in refining petroleum and the alloys which resist their attack at different temperatures are discussed with special reference to nickel-bearing alloys.

The Corrosion of Old Iron Parts Under Water and Underground. G. Schikorr and K. Alex. (Wissenschaftliche Abhandlungen der deutschen Materialprüfungsanstalten, 1941, No. 2, pp. 17-31). An account is given of investigation of the corrosion of iron up to 75 years old which has been recovered from buried positions in Berlin.

The Weather-Resistance of Galvanized Steel Wires and Wire Ropes. G. Schikorr. (Wissenschaftliche Abhandlungen der deutschen Materialprüfungsanstalten, 1944, No. 5, pp. 17-22). The loss in weight by corrosion of galvanized steel wires and wire ropes exposed to the Berlin atmosphere was determined. The corrosion in winter was much greater than in summer and it increased directly with the amount of sulphur in the air. Wire ropes were affected much less than single wires.

Special Pitch for Protection against Corrosion, and Filling Materials Made from German Coal Tars. K. Daeves, H. Klas, and H. Schlumberger. (Korrosion und Metallschutz, 1940, vol. 16, Oct., pp. 339-341). Details are given of "Tepla-Masse," a coal-tar pitch, developed by German tar producers and tube makers, which has excellent properties for protecting the outside of steel tubes against corrosion and bacteria.

Corrosion under Protective Coatings. J. K. Wirth. (Korrosion und Metallschutz, 1940, vol. 16, Oct., pp. 331-338). The "ion-penetration" experiments reported in an earlier paper (see Journ. I. and S.I., 1940, No. II., p. 38 A) have been continued in attempts to establish whether the penetration-resistance effect of the paint film contributes to electrochemical corrosion and whether the thickness of the boundary layer remains constant or increases. Electrical resistance measurements were again made. Clear proof was obtained that the "boundary surface" is actually a "boundary layer" of measurable thickness although the thickness is not uniform. This layer can be only of an oxidic nature on anodically polarized particles of the iron; on cathodically polarized particles the layer must consist of hydrogen. If the current is to flow at all it must penetrate both the oxide and the hydrogen layers. The higher the

ohmic resistance of these surface layers the greater will be the restriction on the current between the base and noble particles of the iron and the less will be the corrosion under the paint.

The Passivating Effect of Active Carbon Saturated with Ammonia. R. v. Wolffersdorff. (Korrosion und Metallschutz, 1940, vol. 16, Oct., pp. 351-354). In an earlier paper P. Prill and E. Böhm have described the beneficial effect of using linseed oil paints containing carbon saturated with ammonia (*see* Journ. I. and S.I., 1940, No. II., p. 36 A). In the present paper further tests are described which illustrate the corrosion-inhibiting effect of paints containing this passivating agent.

The Dependency of the Testing of the Atmospheric Corrosion of Iron on the Uncertainties of the Test Method. G. Schikorr. (Korrosion und Metallschutz, 1940, vol. 16, Dec., pp. 422-427). Atmospheric corrosion tests are described which demonstrate the effects of the following conditions on the results obtained: (1) The roughness of the surface of the specimen; (2) the angle at which it is tilted; (3) the height above the ground; (4) the distance from chimneys; and (5) the time of year.

Full-Scale Tests on the Corrosion of Piles of Copper-Bearing Steel. O. Bauer and G. Schikorr. (Wissenschaftliche Abhandlungen der deutschen Materialprüfungsanstalten, 1941, No. 2, pp. 1-17). A comprehensive account is given of the results of full-scale corrosion tests on steel piling made of steel containing about 0.2% of copper. The test period covers eight years. The piles were exposed to attack by sea water, tidal river water, swamp water, and fresh water. Other tests were made by burying piles in different soils. In swamp water the corrosion rate was 0.05-0.1 mm./year; in river water and three different soils it was 0.005-0.05 mm./year. The copper content had no marked effect on the corrosion resistance.

Stress Corrosion Cracking of Mild Steel. Part IV. Development of the "Free Nitrogen Factor." J. T. Waber, H. J. McDonald, and B. Longtin. (Corrosion and Material Protection, 1946, vol. 3, Feb., pp. 13-16, 24). The theory was developed in Part III. of this series (*see* Journ. I. and S.I., 1946, No. I., p. 70 A) that nitrogen is the principal cause of stress corrosion. The effects of other elements are indirect because they only influence the nitrogen. In this paper the effects of separate elements are combined on a theoretical basis into a single factor called the "free nitrogen factor." It is shown that the extent of ageing and the rate of cracking are strongly influenced by the free nitrogen. The thermodynamics of the numerous reactions between carbon, oxygen, and nitrogen on the one hand and iron, titanium, and aluminium on the other are considered. Finally, the influence of pearlite on the diffusion of nitrogen is shown to be small and negative, *i.e.*, high carbon contents reduce both the ageing and cracking sensitivities of steel.

Stress Corrosion Cracking of Mild Steel. Part V. Development of Experimental Procedure. J. T. Waber

and H. J. McDonald. (Corrosion and Material Protection, 1946, vol. 3, Mar., pp. 13-23). Methods of obtaining stress corrosion cracking in the laboratory are studied and a technique is described in which the specimen has a large area at constant stress available for cracking to develop. The apparatus is also simple and easy to manipulate. The stress distribution in loaded and cracked specimens was determined. The solution used was a mixture of calcium and ammonium nitrates; this is one which gives little general corrosion. The effects of stress and ageing on a number of steels were studied. Ageing usually lowers the stress level at which cracking occurs. Steels loaded at above the yield point crack rapidly, but elastically loaded specimens can be cracked in a reasonable time.

Stress Corrosion Cracking of Mild Steel. Part VI. Verification of Mechanism. J. T. Waber and H. J. McDonald. (Corrosion and Material Protection, 1946, vol. 3, Apr., pp. 13-18). Experiments are reported which show that the removal of nitrogen from steel eliminates the stress-corrosion tendency and the reintroduction of nitrogen restores it. The mechanism of stress corrosion is electrochemical in nature since cathodic protection prevents the growth of cracks. The amount of anodic material decreases with the nitrogen content of the steel; hence the amount of soluble material which controls and causes the stress-corrosion sensitivity increases with the nitrogen content.

Relation of Strain Aging to the Stress-Corrosion Cracking of Mild Steel. J. T. Waber and H. J. McDonald. (Welding Journal, 1946, vol. 25, Apr., pp. 223-S-233-S). A review of the literature on age-hardening, strain-ageing, boiler embrittlement, and stress-corrosion revealed a number of similarities. These similarities are interpreted in the light of the proposed "accelerated precipitation" theory of stress corrosion. Experiments are described in which the removal of nitrogen from steel followed by its reintroduction caused the disappearance and the reappearance, respectively, of the cracking tendency.

Chemical Propellants. Corrosion and Stability Studies. F. Bellinger, H. B. Friedman, W. H. Bauer, J. W. Eastes, and W. C. Bull. (Industrial and Engineering Chemistry, Industrial Edition, 1946, vol. 38, Mar., pp. 310-320). Investigations were made to find suitable containers and materials for storing concentrated hydrogen peroxide and calcium permanganate. Commercial steel drums were found satisfactory for the shipment and storage of permanganates. Concentrated hydrogen peroxide, although stable even at 65° C., is very reactive and it must be carefully protected from contamination. There are only a few materials in which hydrogen peroxide can be stored; of these, aluminium is the best, then come aluminium-magnesium alloys, pure tin, pure tantalum, pure cadmium, and stainless steel; in all cases the surfaces must be conditioned before use.

BOOK NOTICES

(Continued from pp. 15 A-16 A)

ANDRADE, E. N. da C. "*Industrial Research, 1946.*" 8vo, pp. 736. London and New York, 1946: Todd Publishing Co., Ltd. (Price 21s.)

This book is published with the object of assisting all the industries which are contemplating the use of new materials, new processes, new equipment and new types of plant in their factories to obtain better production results. Articles by experienced writers give factual and statistical information in as concise form as possible, emphasizing the importance of industrial science and research.

ARMSTRONG, E. F., and L. M. MIALL. "*Raw Materials from the Sea.*" 8vo, pp. xi + 164. Illustrated. Leicester: Constructive Publications, Ltd. (Price 15s.)

Widespread interest has been aroused by the winning in large quantities on an economic basis first of bromine and then of magnesium as hydroxide from the sea. It is to be expected that other elements will be won directly from the sea in the future; as it is, several are to-day obtained on the land from deposits representing dried up ancient seas or those, like the Dead Sea, which are only partially evaporated.

This book gives an account of the winning of such substances which come either directly or indirectly from the sea, but the authors preface it by a general reference to the chemical problems which the oceans represent and to the various elements present in them in minor quantities. The book is a first effort to bring such information together; it makes no attempt to be exhaustive and is prepared under all the difficulties of war-time conditions.

BRAY, J. L. "*Ferrous Production Metallurgy.*" 8vo, pp. viii + 457. Illustrated. New York, 1942: John Wiley and Sons, Inc.; London: Chapman and Hall, Ltd. (Price 24s.)

This book is devoted solely to the production of iron and steel, and explains the various processes from the physical-chemical standpoint. Simple line drawings, giving only principal parts and dimensions of equipment are included in preference to photographs. It is a companion volume to the author's "*Non-Ferrous Production Metallurgy*" and is intended for use in junior and senior courses of instruction. The chapters cover history, raw materials, the metal iron, the iron blast-furnace, wrought iron, cementation and crucible processes, the Bessemer process, the basic and acid open-hearth processes, the electric furnace, scrap, ingots and ingot moulds, and ferro-alloys. The final chapter is devoted to a survey of the iron and steel industry of the United States.

BUTLER, R. "*The History of Kirkstall Forge through Seven Centuries 1200-1945 A.D.*" La. 8vo, pp. 152. Illustrated. Kirkstall, 1945: Henry Jenkinson, Ltd. (Price 25s.)

The Kirkstall Forge occupies possibly a unique position amongst works of its kind, in that its history goes back some seven centuries, and it has been in operation, in one way or another, during the whole of that period. The present work sets out to sketch the development of the works since its inception, about 1200 A.D., following the construction of a mill race by the Cistercian monks at Kirkstall Abbey, until the present day. The bulk of the history covers the period from the time when the Butler and Beecroft families first became connected with the forge in 1778—a connection which has not yet been terminated—until the beginning of the 1914-1918 war. Although the author's primary aim was to interest people having some connection with the forge, his work has, in fact, a much wider appeal, and should be appreciated by all students

of industrial history, even if they are not chiefly concerned with iron and steel manufacture. The many letters and documents quoted throw a most entertaining light on the relationships between master and craftsman, and between vendors and their clients, particularly in the eighteenth and early nineteenth centuries. In a work of this nature, the enjoyment of the reader is considerably enhanced if it is attractively produced, and in this respect the publishers have certainly not failed. There is a wealth of illustrations, and the quality of reproduction of old photographs and documents is especially noteworthy.

ECKMAN, D. P. "*Principles of Industrial Process Control.*" 8vo, pp. x + 237. New York, 1945: John Wiley and Sons, Inc.; London: Chapman and Hall, Ltd. (Price \$3.50.)

The object of this book is to meet the need, which has arisen as a result of the rapid development of automatic control in industry, for a compact, yet comprehensive treatise on the subject. The scope of the subject is so wide that a book of this size must, as the author points out be regarded as an introduction to the science; and for the most part it is confined to a general discussion of the various types of automatic control in modern industrial processing, rather than a detailed account of individual systems. The treatment is mainly descriptive, but it has been found necessary, at times, to include a mathematical analysis of a process. The lucidity of this exposition is improved by the liberal provision of graphs and line diagrams. As a work of reference for the plant engineer, it will probably not give all the detail required on specific points; but this disadvantage is offset by the useful bibliography given at the end of each chapter. The book should also be of use to the student, in helping to make him aware of an important aspect of his subject which may be neglected by his other text-books. In addition to the ordinary subject index, the author has wisely included a glossary of technical terms.

HEATH, SIR FRANK, and A. L. HETHERINGTON. "*Industrial Research and Development in the United Kingdom. A Survey.*" 8vo, pp. xiii + 375. Illustrated. London, 1946: Faber and Faber, Ltd. (Price 25s.)

This book is a survey of the position of industrial research and development in the United Kingdom up to the end of 1944, and gives an account of the various factors which affect the country's export trade and industrial well-being. It has been written for laymen rather than for experts, but care has been taken to secure the scientific accuracy of the book by consultation with leading authorities while avoiding so far as possible much technical detail. The book is divided into five parts. Part I. contains short descriptions of the leading features which characterize the chief manufacturing industries of the country from an historical and scientific point of view. Part II. deals with research on those activities which serve the citizen as a member of the community. Part III. describes the action taken by the State to encourage or conduct research, with short descriptions of the main activities of various Government departments or of bodies closely allied with the Government. Part IV. contains notes on various important professional and other institutions, the activities of which affect industrial progress, whilst Part V. describes certain general factors affecting that progress in different ways.

MAUGH, L. C. "*Statically Indeterminate Structures.*" 8vo, pp. viii + 338. Illustrated. New York, 1946: John Wiley and Sons, Inc.; London: Chapman and Hall, Ltd. (Price \$5.)

In 1932 Professor Hardy Cross presented engineers with a method of analysing continuous frames which is univers-

ally known to-day by his name or as the moment-distribution method.

This paper marked a revolutionary stage in structural analysis, and since its publication, considerable literature has accumulated dealing with the arithmetical solution of structural problems by methods of successive approximation.

In the book under review Professor Maugh explains and illustrates a number of these methods; in something over 300 pages he discusses the treatment of continuous beams; continuous frames with constant and variable second moments of area; building frames; continuous trusses and bents; elastic arches; rings and frames with curved members and some simple problems connected with the use of flexible members.

A preliminary chapter deals with the fundamental principles of structural mechanics, and a final one with a discussion of such special problems as semi-rigid connections, stresses in space frames and shearing stresses in thin-walled closed sections.

It may be said at once that the book is intended for post-graduate students who have already a sound training in fundamental theory of structures, and to such it should prove valuable, as it collects so many methods into a single volume, and shows their applications to a variety of practical problems. For those who do not already possess such a training, however, the book will probably prove difficult, since the treatment of essential basic theory is often very sketchy, and quite inadequate for a proper appreciation of the subject-matter.

An excellent feature of the work is the inclusion of a large number of numerical examples worked out with complete arithmetical detail, and these should prove of the greatest value to those who are prepared to make a concentrated effort to understand recent developments in structural analysis.

The book is a good example of the technological approach to the study of structures, and will be a valuable addition to the library of advanced students and practising structural engineers.

The production is excellent in every way, and the English reader will note with mixed feelings that it has been "manufactured in accordance with the recommendation of the war production board in the interest of the conservation of paper and other important war materials." The comparison with British books produced under similar needs is so marked that one must envy our American friends their ability to maintain such a high quality of production in technical books.

A. J. S. PIPPARD.

PARKER, H. "*Simplified Design of Structural Steel.*" 8vo, pp. x + 226. New York, 1945: John Wiley and Sons, Inc.; London: Chapman and Hall, Ltd. (Price \$2.75.)

As its title implies, this is an elementary text-book on the design of structural members for use in building construction, and is the fourth of a series of such books on similar subjects. The subject is dealt with in an essentially practical manner, but the derivation of the more simple formulae met with in practice is given, to ensure the student's proper understanding of their application. The book begins with a description of structural sections, and goes on to consider the principles of mechanics as applied to structural design. There are also sections dealing with riveted and welded connections in some detail. The application of mathematical principles is well illustrated throughout the book by the inclusion of worked examples; and there are also problems by which the student may test his own progress. Unfortunately, the solutions to these problems are not given. The author has attempted to make this treatise as self-contained as possible so as to avoid the necessity for the student having to refer to other standard works. To this end, a considerable amount of numerical data, in tabular form, has been included.

SAUNDERS, N. F. T. "*Factory Organization and Management.*" Second Edition. 8vo, pp. viii +

167. London, 1946: Sir Isaac Pitman and Sons, Ltd.

This book deals with the fundamental policy of factory organization and management, and includes chapters on design and development, the drawing office, planning and tooling, control of materials, production and output, buying, handling the finished article, labour problems (including welfare and systems of wage payments), overheads, budgetary control, and estimating and costing. The importance of the human factor is stressed throughout the book.

ZWORYKIN, V. K., G. A. MORTON, E. G. RAMBERG, J. HILLIER, and A. W. VANCE. "*Electron Optics and the Electron Microscope.*" 8vo, pp. xi + 765. New York, 1945: John Wiley and Sons; London: Chapman and Hall, Ltd. (Price \$10.)

The appearance of this book is most opportune, coinciding as it does with the redirection of scientific effort from the problems of war back to those fundamental studies which are the proper domain of the scientist.

The art of electron microscopy is nearly as old as that of the study of surface structure by electron diffraction; and yet the contributions made to new knowledge by electron microscopy are slender compared with the wide fields which have already been opened up by electron diffraction. Why is this?

The answer, it seems to me, lies in the tendency to insist too much on the obvious parallels between optical and electron microscopy. This attitude is so pronounced that many workers have failed to appreciate that, although there is little to be gained in attempting to combine diffraction and microscopy in the wavelength region of visible light, there is every inducement to do so in the case of the electron beam. Indeed, it should be obvious to every thinking worker in the field that the full and certainly wonderful powers of the electron beam as a tool for the study of the fine structure and texture of particles, thin films and surfaces can only be realized by the closest collaboration between the two techniques of electron diffraction and electron microscopy. By this I mean that the electron beam instrument should combine in itself the ability to be able to record the appropriately enlarged image of the object, as well as the diffraction pattern to which precisely that same portion of the object can give rise.

In this book the authors only dimly realize the importance of effectively combining the two techniques. It is true most of the microscopes described can also be used to obtain a diffraction pattern, but in none is the construction and mode of operation such that a true collaboration between the two techniques is achieved, because no proper steps have been taken to ensure that the diffraction pattern and microscope image are formed from identically the same part of the specimen. I do not think, however, that we shall have to wait long for this cardinal advance to be made, and when it has been achieved we shall be able confidently to look forward to the beginning of a tremendous advance in our knowledge of film and surface structure.

The book has been usefully and conveniently divided into a practical and a theoretical section, and in these each chapter has been written by a recognized authority. There is a wealth of useful practical information, and on the theoretical side much has been done to condense and clean up the rather diffuse ramblings of some of the sources drawn from an already extensive literature. The clarity with which fundamental principles have been insisted on by the authors is refreshing and welcome.

There are errors in the book. Some I have pointed out elsewhere and others are of little account; none are likely to confuse the serious user of the book.

I can confidently recommend the book to all present and prospective users of the electron beam in the study of fine texture and structure.

The price, \$10, i.e., £3 in a London bookshop, is an appalling price to pay, even for a book which should be in every scientific library and in the possession of any worker in this branch of electronics. G. I. FINCH.

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FUEL

(Continued from pp. 18 A-19 A)

The Effect of Metals and Metal Oxides on the Decomposition of Carbon Monoxide and Its Technical Importance. W. Baukloh and G. Henke. (Metallwirtschaft, 1940, vol. 19, June 7, pp. 463-470). The manner in which iron and its oxides affect the stability of carbon monoxide at different temperatures is discussed and some laboratory tests in this connection are described. A diagram is presented showing the CO_2/CO ratios and temperatures at which carbon monoxide decomposes in the presence of iron. Iron oxides do not act as catalysts for the $2\text{CO} \rightleftharpoons \text{C} + \text{O}_2$ reaction, but, generally speaking, only the metal itself. Experiments in which carbon monoxide was passed through iron-oxide powder held at 550°C . in an open-ended copper tube resulted in the tube swelling and finally bursting owing to the pressure set up by the carbon deposited within the copper wall.

New Information on Large and Small Gas Immersion Tubes. Part I. Large Gas Immersion Tubes. W. R. Teller. (American Gas Association : Industrial Heating, 1945, vol. 12, Nov., pp. 1906-1918; Dec., pp. 2090-2102). Data and calculations for the design of gas-fired burner tubes for use submerged in baths and tanks are presented. The effective lengths of immersed tube which will supply heat at rates in the range of 10,000-400,000 B.Th.U./hr. with thermal efficiencies of 60%, 70%, and 80% are given.

Quantitative Analysis of Single- and Multiple-Capacity Plants. P. G. Kaufmann. (Proceedings of the Institution of Mechanical Engineers, 1945, vol. 153, pp. 237-246). In order to predict the performance of an automatic regulator it is necessary to know the characteristics of the plant to which the regulator will be applied. It is shown how the behaviour of an uncontrolled plant can be described by a non-homogeneous differential equation of the same order as the number of capacities forming the plant. It is also shown why, for the control of multiple-capacity plants, it may be of advantage to use regulators that respond not only to the deviation from equilibrium but also to the speed and the higher derivatives of the deviation.

On the Theory of Automatic Control : Regulator Equations. P. G. Kaufmann. (Proceedings of the Institution of Mechanical Engineers, 1945, vol. 153, pp. 249-257). It is shown how different types of automatic regulators can formally be characterized by their regulator equation. These are differential or integral equations between the displacement of the power device, its speed and higher derivatives, on one side, and the deviation from normal of the controlled variable and its derivatives, on the other side.

Automatic Furnace Control. (Iron and Steel, 1946, vol. 19, June, pp. 395-396). A description is given of a furnace control apparatus which operates a solid-fuel furnace entirely automatically with the precision associated with gas-firing both in temperature and atmospheric conditions.

Experimental Gas Turbine Plant. (Engineer, 1946, vol. 182, July 19, pp. 51-53). A description is given of an experimental gas turbine unit designed for a net output of 500 h.p. at 6000 r.p.m. the construction of which was commenced in 1938. Brief details are also given of a gas turbine to run at 300 r.p.m. designed for driving a blast-furnace blower.

Heat Transfer through Tubes with Integral Spiral Fins. D. L. Katz, K. O. Beatty, jun., and A. S. Foust. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 665-672). Heat-transfer data for a group of tubes having integral spiral fins are presented and discussed. The group includes tubes with from 4 to 24 fins/in. with fin heights ranging from 0.05 to 0.38 in. The performance of tubes with fins is compared in all cases with that of plain tubes tested under similar conditions.

Heat Transfer and Pressure Loss in Small Commercial Shell-and-Finned-Tube Heat Exchangers. R. M. Armstrong. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 675-681). Preliminary results are submitted covering heat transfer and pressure loss for fluids flowing through the shells of small shell and finned-tube heat exchangers in cross-flow. These results are compared with the calculated performance of similar exchangers with bare tubes.

Heat-Transfer Coefficients and Other Data on Individual Serrated-Finned Surface. E. A. Schryber. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 683-686). Heat-transfer data from tests on tubes with serrated fins are presented and discussed. The tubes are easy to fabricate and it is a simple matter to alter the ratio of the finned surface to the tube surface.

Disk-Extended Surfaces for High Heat-Absorption Rates. G. E. Tate and J. Cartinhour. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 687-692). Four types of heat exchangers with tube surfaces extended by discs are discussed, namely : (1) Interlocking cast-iron sections of nine discs each; (2) die-cast aluminium-alloy discs; (3) two surfaces die-pressed from wrought iron sheet, each with a flue; and (4) a sixteen-pronged star-shaped fin. Details are given of the testing procedure for these tubes, together with their rates of heat absorption.

Numerical Methods for Transient Heat Flow. G. M. Dusingberre. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 703-710). This paper deals with the application of mathematical methods for the solution of heat-conduction problems.

Heat Transfer through Extended Tube Surfaces. (Engineering and Boiler House Review, 1946, vol. 60, Mar., pp. 66-72; Apr., pp. 106-110). Papers presented at a recent meeting of the Heat Transfer Division of the American Society of Mechanical Engineers are reviewed; they deal with the transfer

of heat from flowing gases to new types of finned tubes.

"Waste Heat" Recovery in the Iron and Steel Industry. P. O. Rosin. (Institute of Fuel Conference on Industrial "Waste Heat" Recovery, 1946, Apr., pp. 9-10). It is pointed out that regenerators return only heat which disappears anyhow in the open-hearth furnace operation and that this is of low-temperature value, whereas 60% of the high-temperature heat is lost. There are two principal means of reducing the latter loss. First, by insulation, and secondly, by reducing the time of operation. The useful portion of heat is related to output and is constant for a given size of charge, whilst the dissipated portion is related to time. Under present conditions a reduction in time of 10% would lead to a fuel saving of about 6%.

Waste Heat Recovery in the Metallurgical Industry. E. C. Evans and A. H. Leckie. (Journal of the Institute of Fuel, 1946, vol. 19, June, pp. 166-175). The design, advantages and limitations of recuperators and regenerators are comprehensively reviewed. The latter reign supreme in melting furnaces, whilst the former are finding increasing applications in reheating and heat-treatment furnaces.

The Missing Data on Coal Sampling. B. A. Landry. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 69-79). This paper is devoted to classifying missing data on coal sampling which are intended to supply information on: (a) Composition; (b) variability of ash of pieces by a float-and-sink method and by direct analysis; (c) variability of ash and increments; and (d) collection and analysis of gross samples of a specified number of increments of constant weight to give confirmation of established relations between the variables involved.

The Preparation and Utilisation of Coal. J. Crossland. (Institute of Fuel Bulletin, 1946, June, pp. 201-203, 209). Difficulties in the preparation of coal in Great Britain which are the concern of the colliery management rather than the fuel technologist are discussed.

Recent Improvements in Coke Oven Design and Operation. L. N. Wilputte and F. Wethly. (Blast Furnace and Steel Plant, 1946, vol. 34, Mar., pp. 355-367). The advantages and disadvantages of several types of charging car for coke-ovens and the effect of the number and position of the charging holes are discussed; steps to improve coke-oven operation are considered. A charging car is described which ensures no spilling of coal and reduces the charging time and the number of strokes of the levelling bar. A design of flue to prevent the formation of roof carbon is described. It is recommended that the thickness of the brickwork over the ovens be increased from 3 ft. 3 in. to 4 ft. 6 in.

Use of Anthracite Fines in By-Product Coke Production. J. D. Clendenin, K. M. Barclay, and C. C. Wright. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 405-415). The blending of Pennsylvania anthracite with coking coals as a means of mitigating the acute shortage of certain types of metallurgical coke has received considerable attention and an attempt is made in

this paper to evaluate, at least relatively, some of the variables encountered when using these anthracite fines. Factors influencing the suitability of different anthracites for blending purposes are discussed.

Blending Coals Reflects Greater Uniformity of Product. R. F. Stilwell. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 417-424). The equipment and processes for blending coals to obtain a suitable mixture for coke-making are described and discussed.

Beneficiation of Blast Furnace Coke at the Kaiser Steel Company, Fontana, Cal. J. H. Thompson. (Eastern States Blast Furnace and Coke Association of the Chicago District: Blast Furnace and Steel Plant, 1946, vol. 34, Feb., pp. 225-230; Mar., pp. 350-354; Apr., pp. 475-479; May, pp. 584-586, 624). Various processes for the beneficiation of blast-furnace coke at the Fontana works are discussed, and methods of sampling and testing are described. The coals used (from Utah) were known to make a weak coke and to be subject to degradation in storage, requiring special stocking methods. Alterations to coke screens and bins resulted in an immediate increase in coke yield and a decrease in the yield of breeze, whilst the chemical and physical properties of the coke were improved by coal preparation and washing, and the addition of coal-tar pitch. Further improvement in coke strength and coke yield, and improved performance and decreased coke consumption at the blast-furnaces, were achieved by the addition of Oklahoma low-volatile coals to the normal Sunnyside blend, the amount finally adopted being 12½%, but, although the coke produced was suitable, the high freight charges for the Oklahoma coals consequent upon the 1500 miles' rail haulage were a consideration. Previous work at various plants had indicated that low-temperature char can serve as a substitute for low-volatile coals, and it was thought that such char made from Sunnyside or some other comparatively near-by coal might give results as good as those obtained with the Oklahoma-Sunnyside mixture. Tests showed that considerable improvements were obtainable by the use of 5-10% of low-temperature char and that Sunnyside coal would blend with its own such char. In further tests, conducted in a full-size oven, a 24.5% improvement in coke quality—as measured by the physical fuel value index—was obtained, compared with a 28% improvement when using 12½% of Oklahoma coal. In view of these results a pilot plant for the production of 500-1000 lb. of low-temperature char per 2-hr. batch was constructed. The effects of various proportions of char in the blend are tabulated and results indicate that with 15% of char a slightly better coke is obtained than with 12½% of Oklahoma coal. It is claimed that in the low-temperature char process a yield of at least 25 gal. of low-temperature by-product tar is obtained per ton of coal. With the present credit for this tar (\$0.07/gal.), the cost of the char is about \$1.30 above that for Sunnyside coal. With a credit of \$0.10/gal., the costs for char and coal will be about equal; if higher percentages of tar acid oils were extracted during the process, the credit of \$0.10/gal. could be exceeded. A survey is made of the effect of oven

width, oven temperatures, and speed of coking, and the paper concludes with a comparison between the optimum volatile content for Fontana and Colorado low-temperature chars.

"Waste Heat" Recovery in the Carbonizing Industries. S. Pexton. (Institute of Fuel Conference on Industrial "Waste Heat" Recovery, 1946, Apr., pp. 11-13). Advances in the technique of waste-heat recovery which are of immediate practical application to new projects in the carbonizing industry are discussed.

Gas-Producer Plant at Hadfields' East Hecla Works. (Iron and Coal Trades Review, 1946, vol. 153, July 5, pp. 11-13). An illustrated description is given of a new gas-producer plant at the works of Hadfields, Ltd. It consists of three Wellmann-Galusha producers capable of producing a total of 525,000 cu. ft./hr. of gas at N.T.P., with coke-handling and gas-cleaning plants, the latter comprising a pre-cooler, disintegrators, spray separators, and oxide boxes.

The Operation of Gas Producers. (Ministry of Fuel and Power, 1946, July, Fuel Efficiency Bulletin No. 44: H.M. Stationery Office). A comprehensive account of gas-producer operation is given in a manner easily read by both operative and superintendent, the object being to promote more efficient working.

Shale Fuels for Iron Production. S. Bergh. (Jernkontorets Annaler, 1946, vol. 130, No. 5, pp. 171-178). (In Swedish). The possibilities of using oil and gas derived from shale for Swedish iron and steel

works are examined. The richest shale deposits at Närke lie in the centre of a fuel-consuming industrial district. By the Bergh process, which was fully tested during the war, it is possible to produce oil and a rich fuel gas at prices which, on a calorific basis, are approximately the same as the pre-war figure for imported oil. These two fuels could be delivered at the works at a price equivalent to that of coal at 40 Kr. (48s. 4d.) per 1000 kg. With a capital outlay of about £900,000 a shale-oil plant could be constructed capable of producing annually oil equivalent to 30,000 metric tons of coal and gas equivalent to 20,000 metric tons of coal. The shale-oil plant would operate as an auxiliary plant of the iron and steel works; it would require a few men of high technical ability, but it would not need any large laboratories or other costly services.

Peat Coal as Fuel for Generating Gas. W. W. Hintze. (Jernkontorets Annaler, 1946, vol. 130, No. 5, pp. 193-198). (In Swedish). Owing to the fuel shortage in Sweden peat has been used in gas producers and it has also been carbonized to make "peat coal". A short account is given of gas-producer trials in which the effect of mixing these two fuels in different proportions on the properties of the gas was studied. The calorific value of the gas was improved to the value of that obtained in a bituminous-coal-fired producer by increasing the proportion of peat coal, and the gas was also very low in sulphur.

PRODUCTION OF IRON

(Continued from pp. 19 A-20 A)

Proceedings of the Blast Furnace and Raw Materials Conference. (American Institute of Mining and Metallurgical Engineers, Blast Furnace and Raw Materials Conference, Apr., 1944). The proceedings of the Annual Conference of the Blast Furnace and Raw Materials Committee of the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers, held at Pittsburgh on April 20 and 21, 1944, are reported. The Conference was divided into four sessions dealing respectively with coking coals and coke, iron ores, sintering and blast-furnace filling, and ore and coal bedding.

In the first session B. P. Mulcahy discussed the way in which the characteristics of the coal charged and the coke-oven practice affect the physical properties of the coke such as size, strength, weight per cubic foot, porosity, and cell size. In the second paper of this session J. A. Kelley reported on the revival of coke manufacture in beehive ovens to meet the heavy demand for coke, especially in 1942 and 1943. Details of the process are given and the effects of beehive coke on the blast-furnace process are considered.

In the first paper of the second session C. V. Firth described a process for agglomerating fine iron ore into hard, porous balls which are equivalent in structure, reducibility, and resistance to abrasion to the best types of furnace ore. The process is similar

to the Gröndal process. In the former the damp ore is moulded into balls in a rotary drum and the balls are then heated in a vertical shaft furnace to a temperature below fusion. The equipment at the Bureau of Mines Experiment Station for moulding the balls and the 35-ton furnace are described. The results of tests on the product are reported and a theory is put forward to account for their characteristics. Tentative designs for a circular 200-ton furnace are presented. In the second paper of this session T. L. Joseph and G. Bitsianes compared the properties of iron ore, sinter, and ore nodules as blast-furnace charging materials, giving data on their heat capacities and reducibilities. In the third paper of this session T. B. Counselman reviewed new developments in the beneficiation of iron ores in the United States (see Journ. I. and S.I., 1945, No. II., p. 28 A).

M. F. Morgan began the third session with a paper on sintering-plant practice in which he dealt at length with the raw materials, design of plant and equipment, and the operating procedures. The second paper of this session was entitled "Some Factors Affecting Distribution of Stock in the Blast-Furnace Top" in which T. J. Wells described investigations to determine whether beneficial changes could be made to a blast-furnace with an 11-ft. 8-in.

dia. hearth at the works of the Steel Company of Canada, Limited. The paper dealt in particular with the manner in which the stock contour is affected by the plasticity of the ore, the bell clearance and the speed at which the bell is moved.

The final session consisted of one paper, "Blending of Bulk Materials" in which J. F. Meissner discussed several methods of storing and collecting bulk materials with the object of evening out fluctuations in their composition or quality. Special attention is given to the Robbins-Messiter bedding system. Horizontal, vertical, and inclined layer systems in bins and silos are also considered.

The discussions which followed each of the papers are also reported.

The Use of Scrap in the Blast Furnace. K. Neustaetter. (Blast Furnace and Coke Association of the Chicago District: Blast Furnace and Steel Plant, 1946, vol. 34, May, pp. 592-593, 595-599, 627, 631-632). Methods of charging various types of scrap into the blast-furnace, in amounts of up to 10% of the total burden, are described, and the effects on furnace performance are discussed. Suggestions are made for the obtaining of the maximum benefit from the use of scrap in the charge.

The Blast-Furnace Process and Means of Control. T. L. Joseph. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 2021: Metals Technology, 1946, vol. 13, Apr.). The major obstacles to greater efficiency and control in the blast-furnace process centre around the problem of obtaining a more ideal counter-flow of gases and solids. The effects of furnace size, blast temperature, and beneficiation of raw materials are discussed, and data obtained from actual practice and experiments with models are presented and reviewed.

Determining Rates of Deoxidation of Iron Oxide Materials in Reducing Gases. E. P. Barrett and C. E. Wood. (Industrial and Engineering Chemistry, Analytical Edition, 1946, vol. 18, May, pp. 285-286). An apparatus and procedure for determining the rates of deoxidation of iron oxide materials in reducing gases are described.

The Influence of the Chemical Composition on the Temperature-Viscosity Relationship of Acid Blast-Furnace Slags. K. Endell and R. Kley. (Iron and Steel Institute, 1946, Translation Series No. 280). This is an English translation of a paper which was published in *Stahl und Eisen*, 1939, vol. 59, June 8, pp. 677-685. (See *Journ. I. and S.I.*, 1939, No. II., p. 133 A).

The Effect of Silica, Titania, and Alumina on the Viscosity of a Synthetic Acid Slag, and the Calculation of the Viscosity of Acid and Basic Blast-Furnace Slags from the Chemical Composition. K. Endell and G. Brinkmann. (Iron and Steel Institute, 1946, Translation Series No. 281). This is an English translation of a paper which was published in *Stahl und Eisen*, 1939, vol. 59, Dec. 7, pp. 1319-1321. (See *Journ. I. and S.I.*, 1940, No. I., p. 127 A).

Ferro-Alloy Manufacture and Use. (British Intelligence Objectives Sub-Committee, 1945, Fiat Final Report No. 485: H.M. Stationery Office). A review is presented of the methods used in Germany for making ferro-alloys and calcium carbide.

Selective Reduction of Iron in Chromite by Methane-Hydrogen and Similar Gas Mixtures. F. S. Boericke. (United States Bureau of Mines, 1946, Report of Investigations 3847). The continuous reduction of chromite ore with methane-hydrogen mixtures was studied in more than 60 small-scale tests. The rate of reduction of the iron oxides present by methane was extremely high and this reduction could be carried out at 1000-1100° C. instead of at 1300° C. which is the roasting temperature required when carbon is the reducing agent.

The Höganäs Sponge Iron Process. S. Eketorp. (Iron and Steel Institute, 1946, Translation Series, No. 275). This is an English translation of a paper which appeared in *Jernkontorets Annaler*, 1945, vol. 129, No. 12, pp. 703-721. (See *Journ. I. and S.I.*, 1946, No. I., p. 38 A).

Case Hardening of Sintered Steel. G. Stern and J. Greenberg. (Powder Metallurgy Bulletin, 1946, vol. 1, Mar., pp. 18-23). **Heat Treating Carburized Sintered Steel.** G. Stern and J. Greenberg. (Iron Age, 1946, vol. 157, Apr. 25, pp. 56-61). An investigation is described in which the effects of various carburizing methods and subsequent heat-treatments on the depth, hardness, and micro-structure of the case of three powder-metallurgy products and (for comparison) a cold-rolled bar of S.A.E. 1015 steel were investigated. The powder-metallurgy specimens were made with (a) reduced iron powder containing a little copper, (b) electrolytic iron powder, and (c) electrolytic iron powder with 1% of manganese added in the form of ferromanganese. Pack-carburizing and gas-carburizing resulted in approximately the same hardness and case depth when applied at the same temperature. The results obtained with the powder-metallurgy specimens were very similar to those with the cold-rolled bar.

FOUNDRY PRACTICE

(Continued from pp. 20 A-22 A)

Basic Principles of Cupola Operation. R. A. Clark. (American Foundrymen's Association: Foundry, 1946, vol. 74, June, pp. 102, 298-301). The reactions taking place in the cupola are explained and it is shown how these are affected by changes in the volume of blast and in the size of the coke. The differences in the zones traversed by metal lying near

the cupola wall and close to the centre are pointed out and recommendations for obtaining a product of uniform quality are made.

Second Report on the Basic Cupola. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 79, July 4, pp. 239-242). Since the publication of the First Report on the Basic Cupola (see *Journ. I.*

and S.I., 1945, No. I., p. 44 A), the Basic Cupola Sub-Committee was appointed to study dephosphorization and details of its investigations are now published in the Second Report. The experiments described confirm that some dephosphorization can be obtained during melting in a basic-lined cupola. The abnormally high pick-up of carbon reported by Heiken is confirmed and it was found that appreciable desulphurization can be obtained simultaneously with dephosphorization. With high steel charges of the type used in the cupola-converter process there is no difficulty in producing conditions under which phosphorus may be removed, but with this type of charge there is a serious danger that such conditions will result in the production of metal unsuitable for further processing. As the plants in which this experimental work was done are no longer available, the possibility of desulphurizing and dephosphorizing in basic-lined ladles is being examined. The Sub-Committee consider it very important that work on the development of a satisfactory basic cupola process should continue.

Developments in Gray Iron and Malleable. G. Vennerholm. (Metal Progress, 1946, vol. 49, June, pp. 1163-1168). A review of the wartime improvements in the properties of grey iron and malleable cast iron and in the production and processing of these materials is presented.

Who Discovered Black Heart Malleable? H. A. Schwartz. (Foundry, 1946, vol. 74, May, pp. 175, 302-306). The history of the manufacture of the first black-heart malleable cast iron is examined and the possible origin of three halberds of malleable iron found in North America and used in the fifteenth century is discussed.

The Technique of Casting Steel. A. Heuvers. (Iron and Steel Institute, 1946, Translation Series No. 279). This is an English translation of a paper which was published in *Giesserei*, 1943, vol. 30, Sept., pp. 201-209. (See Journ. I. and S.I., 1946, No. I., p. 19 A).

Experimental Work on the Production and Use of Radiographed Steel Castings for Service at High Pressures. F. H. Keating. (Iron and Steel Institute, 1946, this Journal, Section I). The paper describes a practical experiment in the production of castings for use in handling fluids at 350-atm. pressure. The castings selected for the experiment were of such size and form as to lend themselves to production and radiography by existing equipment. The paper discusses the economic and technical advantages attending the use of castings for this class of duty, and emphasizes that the principal deterrent to their widespread use in this way is the uncertainty as to the soundness of a casting. The use of radiography to provide the necessary assurance on soundness is tested on a number of castings, and the results of the practical experiments are analysed. Castings which passed the stringent acceptance tests were installed on high-pressure lines and their performance is under observation. A trial period of two years in service is visualized before any definite conclusions can be drawn. The experiments described in the paper utilized very extensive radiographic examination of all castings produced. Such extensive and costly

examination was considered justifiable and necessary for the first experimental castings, but a reduction in the extent of radiographic examination is considered essential for commercial development. The author visualizes that such reduction may be obtained by careful standardization of moulding and casting methods for each size and type of casting. Such standardization may eventually permit of the acceptance of castings which have been radiographed only in key positions. Further investigation along these lines is contemplated on completion of the trial period of two years' service.

Electronic Melting Furnace Facilitates Injection Molding of Steel. S. M. Milanowski. (Steel, 1946, vol. 118, May 27, pp. 86-87, 128-130). A description is given of an injection type of casting machine for producing accurately finished steel castings weighing up to about 15 lb. The molten steel is supplied from a high-frequency induction furnace and a ram with a tungsten-carbide face forces it through a nozzle $\frac{3}{8}$ in. in dia. into the metal dies. The ram and one half of the metal mould are moved by hydraulic power.

Sand Problems in the Casting of Steel. S. H. Ljunggren. (Iron and Steel Institute, 1946, Translation Series No. 271). This is an English translation of a paper which was published in *Jernkontorets Annaler*, 1945, vol. 129, No. 8, pp. 457-517. (See Journ. I. and S.I., 1945, No. II., p. 159 A).

High Temperature Sand Testing. D. C. Williams. (American Foundryman, 1946, vol. 9, Feb., pp. 55-59). A brief description is given of a newly constructed furnace intended for research on the hot-compressive and hot-transverse strengths of foundry-sand test-pieces at elevated temperatures. Curves for the green-compressive-strength/exposure-time ratio and data for eight sand mixtures (containing different amounts of western and southern bentonites, fireclay, and cereal and silica flours) having a moisture content of 5% are shown for temperature control settings of 1600°, 2000°, and 2500° F. The investigation involved the testing of 1119 specimens, and results are given in tables.

Foundry Sand Control Plan. H. W. Dietert. (Foundry, 1946, vol. 74, June, p. 113). A chart is presented which gives in concise form the measures to take in order to prepare foundry sand so that it complies with certain specified requirements.

Patterns in the Jobbing Foundry. W. C. Manwell. (American Foundryman, 1946, vol. 9, Feb., pp. 30-36). Some practical problems relating to patterns in foundry operation are considered, and the following items are discussed: Split patterns; the problem of loose pieces on patterns and in core boxes; care in the use and placing of dowel pins; the provision of draw-straps; the design of large patterns; the design and use of core prints; the question of fillets; the use of an old casting as a pattern; shrinkage; the use of shellac and standard colours. The value of co-operation between the patternmaker and the foundryman is pointed out.

Closer Co-operation between the Foundry and the Pattern Shop. W. C. Meredith. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 79,

May 2, pp. 3-4; May 16, pp. 49-52). Examples of good and bad pattern-making are cited and a plea is made for better organization of pattern-shop work which should include the supply of adequate information to the pattern shop.

Is the Pattern Shop an Asset or a Liability? H. Padley. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 79, May 23, pp. 83-87, 92). The equipment and layout of a good pattern shop are described. Details are given of the individual machine used, especially the universal pattern miller. Some examples of good patterns are described.

Cores for Sale. E. F. Ross. (Foundry, 1946, vol. 74, Apr., pp. 87, 198-200). A description is given of the production methods developed by a Chicago company specializing in making cores for foundries in the district.

Blowing Cylinder Barrel Cores. A. H. Allen. (Foundry, 1946, vol. 74, May, pp. 170-173, 288). A detailed description is given of core-blowing machinery and equipment for the rapid production of crank-case barrel cores for 8-cylinder Buick engines.

Baking Cores Dielectrically. J. McElgin. (Foundry, 1946, vol. 74, June, pp. 114-116, 288-290). The advantages of the high-frequency process of baking cores made with synthetic-resin binders are pointed out and the equipment with which this is done is described.

Rapid Baking of Foundry Cores by Dielectric Heating. R. T. Wise and J. P. Moran. (Materials and Methods, 1946, vol. 23, May, pp. 1307-1316). The advantages of employing dielectric heating for

baking cores are pointed out. One of the heating units illustrated is capable of baking approximately 360 lb. of cores/hr. with a consumption of 25 kW.

The Technique of Composite Casting. E. Knipp. (Metallwirtschaft, 1940, vol. 19, May 24, pp. 421-424). Descriptions and examples are given of methods of composite casting so as to make, for example, a bronze bearing surface on a steel shell, or a manganese-steel wear-resisting surface on a grey cast-iron block.

Elevating Trucks in the Foundry. R. S. Turner. (Foundry Trade Journal, 1946, vol. 79, June 27, pp. 225-227). Methods of solving internal transport problems in foundries are described with special reference to a tipping skip (called a "stillage") which is supported on a frame on wheels such that the elevating mechanism of a petrol driven truck can be brought underneath it so as to raise it off the ground and transport it to any other part of the foundry.

Ventilating the Mold Shakeout. C. C. Hermann. (Foundry, 1946, vol. 74, June, pp. 117, 274-278). This article forms the second part to a previous one on the design of ventilating equipment for foundries (see p. 22 A). Details of the design of down-draught ventilators and double canopy hoods are discussed.

Gray Iron Foundry Conditioning. C. W. Schwenn. (Gray Iron Founders' Society: Foundry, 1946, vol. 74, June, pp. 104-108, 260). An account is given of the cost and benefits obtained by improving the appearance, cleanliness, and working conditions in a large grey iron foundry.

PRODUCTION OF STEEL

(Continued from pp. 22 A-23 A)

Some Developments in the Iron and Steel Industry. A. G. Robiette. (Institute of Metals: Metal Treatment, 1946, vol. 13, Summer Issue, pp. 99-107, 118). Beginning with ore beneficiation, recent developments in all phases of the iron and steel industry are surveyed and the paper ends with some notes on recent fundamental research.

Metals and Metallurgy in the Twentieth Century. G. H. Stanley. (Journal of the Chemical, Metallurgical and Mining Society of South Africa, 1946, vol. 46, Mar.-Apr., pp. 235-263). A comprehensive account is presented of the progress which has taken place in the principal metallurgical processes since 1900.

Conservation of Utilities in Republic's Canton Plant. P. L. Walter. (Iron and Steel Engineer, 1946, vol. 23, May, pp. 39-49). Details are given of the measures adopted by the Republic Steel Corporation to effect economies in the production of electricity, steam and fuel, and in the use of water and air.

The German Ball and Roller Bearing Industry. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 346: H.M. Stationery Office). An account is given of the wartime activities and present position of the German ball- and roller-bearing industry.

Progress in Open Hearth Furnace Construction and

Operation. J. O. Griggs. (Blast Furnace and Steel Plant, 1945, vol. 34, Apr., pp. 480-481, 483-486). A review is presented of improvements in the design of American open-hearth furnaces from 1869 to the present time.

Aid to Control of Open Hearth Practice by Statistical Methods. R. E. Dienst. (Iron and Steel Engineer, 1946, vol. 23, May, pp. 68-74). Several graphs are presented which indicate the relationship between various factors in open-hearth steelmaking practice. The use of these and statistical methods to detect the causes of low production or poor quality is explained.

The Use of Graphite for Reboiling Soft Melt Heats. R. Russell Fayles. (Blast Furnace and Steel Plant, 1946, vol. 34, Apr., pp. 52-54, 78-81). A "soft melt" is a heat so low in carbon on the initial carbon test that additional carbon must be added to the bath during the refining period. The use of amorphous Mexican graphite containing 87% of carbon as the addition agent is discussed. This can be introduced into the bath without undue reaction with carbon recovery efficiencies of 55-80%. Its advantages as compared with pig-iron additions for the same purpose are pointed out.

Ladle Reactions in Rimmed Steel. F. G. Norris and E. B. Hughes. (Iron Age, 1946, vol. 157, June 6,

pp. 72-76). Ladle reactions during the pouring of ingots with rimming steel are considered. In particular the interrelationship of such factors as the ferrous oxide content, the fluctuations in the carbon content, the movement of manganese from metal to slag, and ferrosilicon additions are examined and correlated statistically.

Openhearth Bottom Repairs. J. B. McIntyre. (Iron Age, 1946, vol. 157, May 23, pp. 62-64). A description is given of a mechanical device for extracting liquid steel from cavities in the hearth of an open-hearth furnace to facilitate bottom repairs. It consists of a refractory-lined air-tight box about $4 \times 2 \times 2$ ft. which is held by the charging machine; a refractory-lined steel tube 15 ft. long extends from the front of the box; the front end of this tube is bent down so as to pass through the furnace door and dip into the cavity. A vacuum pump, also mounted on the charging machine, is connected to the top of the box and this supplies the necessary suction to draw the steel from the cavity into the box.

Manufacture and Application of Specialized Magnetic Materials Generally (Including Notes on Other Alloys Requiring Similar Manufacturing Technique). (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 8: H.M. Stationery Office). A report is presented on developments in Germany relating to magnetic materials, improvements in manufacturing methods, and the application of such materials. Other alloys used in electronics and produced by special metallurgical operations are also dealt with.

Carbon Electrodes, I.G. Farben, Griesheim. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 258: H.M. Stationery Office). A description is given of the methods of manufacturing carbon electrodes employed by the I.G. Farbenindustrie, Griesheim, where 2000 tons of electrodes of a great variety of sizes and forms were made per month up to March, 1945.

German Carbon Electrode Manufacture at Griesheim (I.G.F.). (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 338: H.M. Stationery Office). The report deals with the raw materials, plant, and process for the production of the paste used in making large carbon electrodes at the I.G. Farbenindustrie factory at Griesheim, Frankfurt. It includes descriptions of a self-firing calciner and a large extrusion press.

An Equilibrium Study of the Distribution of Phosphorus between Liquid Iron and Basic Slags. T. B. Winkler and J. Chipman. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1987: Metals Technology, 1946, vol. 13, Apr.). A series of experimental heats was made in an induction furnace to study the factors controlling the distribution of phosphorus between a molten iron bath and a basic slag at equilibrium. A value for the dissociation constant of calcium orthosilicate at steelmaking temperatures was determined and an equilibrium constant for the dephosphorization of molten iron by a basic slag was calculated. The effect of slag composition on the activity of iron oxides

in the slag and on the free lime content of the slag is illustrated in ternary diagrams. Dephosphorization was found to be improved by: (a) decreasing the temperature, (b) increasing the iron oxide content of slag and metal, and (c) increasing the basicity of the slag with lime or magnesia.

Sulphur Equilibria between Liquid Iron and Slags. N. J. Grant and J. Chipman. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1988: Metals Technology, 1946, vol. 13, Apr.). Many experimental heats were made in an induction furnace to study the equilibrium distribution of sulphur between the metal and various slags ranging from strongly basic to slightly acid. In the range of slags investigated it was concluded that: (1) MnO and MgO on a mol. per mol. basis are as good desulphurizing agents as CaO; (2) fluor spar is neutral and does not affect the ratio $(S)/[S]$ (*i.e.*, sulphur in the slag to sulphur in the metal); (3) changes in temperature within the 1540-1660° C. range do not affect the above ratio; (4) if the temperature rises above 1660° C. this tends to increase the sulphur in the metal, whilst temperatures below 1540° C. and/or less than 3% of FeO tend to improve desulphurization; and (5) sulphur equilibrium is closely approached during refining in the open-hearth furnace, and in low-carbon heats the value of $(S)/[S]$ reaches its maximum at about 8.

Some Statistical Studies of Surface Quality Controls. H. J. Forsyth. (Blast Furnace and Steel Plant, 1946, vol. 34, Apr., pp. 469-474, 479). Statistical investigations are described which were undertaken to evaluate the effects of steelmaking, ingot-mould preparation, soaking-pit practice, and blooming-mill practice on the occurrence of surface defects in billets.

Dissociation Reactions within Inclusions. C. A. Zapffe. (Iron and Steel Institute, 1946, this Journal, Section I). This paper draws attention to two types of fine-scale phenomena operating within non-metallic inclusions which in some cases have an important effect on the metal. *Intrinsic* reactions (the first type) are based upon the existence of low-valence non-metallic forms at steel-melting temperatures. Thermodynamically, such systems are isolated, and the compounds spontaneously dissociate during cooling—regardless of the chemical nature of the matrix—into higher-valence compounds plus free elemental metal which may enrich the surrounding steel by dissolving in it. Analogous to the graphitizing of carbon monoxide on cooling, evidence is presented of “siliconizing” in iron-silicon alloys and cast steel, and of “chromizing” in stainless steel, this evidence being based on the high-temperature protoxide forms of silicon monoxide (SiO) and chromium monoxide (CrO), respectively. *Extrinsic* reactions (the second type) involve included phases which are chemically interdependent with the matrix and are therefore not isolated in a thermodynamic sense. During thermal changes such systems can lead to local redistribution of alloying elements between inclusion and matrix, and the manner in which this takes place may have an important effect on the service or properties of the steel. “Sensitizing” in austenitic stainless steels is one example; and the phenomenon of “flash attack”

in certain chromium steels is suggested as another example of commercial importance.

The Training of Metallurgical Engineers in the Steel Industry. E. C. Wright. (American Institute of

Mining and Metallurgical Engineers: Mines Magazine, 1946, vol. 36, Feb., pp. 75-76). Recommendations are made on the training of steel plant engineers.

FORGING, STAMPING, AND DRAWING

(Continued from pp. 23 A-24 A)

Press Tools for the Production of Sheet Metal Door Frames. (Sheet Metal Industries, 1946, vol. 23, June, pp. 1156-1158). Recommendations are made on the design of dies and sequence of processes for pressing sheet metal into two special sections for making door frames.

Stampers Benefit from Developments in Modern Press Design. (Steel Processing, 1946, vol. 32, Mar., pp. 168-170). Some modern types of hydraulic press are described and illustrated.

Forging Die Design. J. Mueller. (Steel Processing, 1946, vol. 32, Mar., pp. 174-177; Apr., pp. 244-247). Trimming punches and dies for removing the flash from cold and hot forgings are described.

Designing, Drafting, and Using Press Tools. C. W. Hinman. (Steel Processing, 1946, vol. 32, Apr., pp. 239-243). The design of two-station perforating and blanking dies is discussed with notes on the operation of such dies.

Selection of Cold Work Die Steels. G. M. Butler. (American Society of Tool Engineers: Steel Processing, 1946, vol. 32, Apr., pp. 229-233). Details are given of the properties of water-hardening, oil-hardening and air-hardening die steels for cold-pressing, and

recommendations on their selection for particular work are made.

The Friction Properties of Various Lubricants at High Pressures. J. Boyd and B. P. Robertson. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 51-56). An investigation was made of the friction-reducing properties of various special lubricants used under high pressure for pressing and punching. The lowest value of the average coefficient of friction was obtained with stearic acid; this value was 0.022.

Deep Drawing of Steel Tubs. (Steel Processing, 1946, vol. 32, Mar., pp. 161-163). A description is given of the deep-drawing operations in the manufacture of steel tubs for washing machines. These tubs are 16 in. deep and they are pressed from blanks of enamelling steel 44 in. in dia. \times 18 gauge.

Reactive Wire Drawing. III. Janet M. Howden and R. W. Lunt. (Wire Industry, 1946, vol. 13, June, pp. 329-330). Further consideration is given to the increase in die life obtainable by the reactive drawing of wire (*see* Journ. I. and S.I., 1946, No. I., p. 43 A). A die life factor and a formula for estimating die life in relation to the interfacial pressure between the wire and the die channel wall are developed.

ROLLING-MILL PRACTICE

(Continued from pp. 24 A-25 A)

Electrical Power Supply for Steel Mill Loads. F. W. Cramer. (Iron and Steel Engineer, 1946, vol. 23, May, pp. 55-59). The factors affecting the selection of an electric power system for an integrated iron and steel works producing 125,000 tons of ingots per month are discussed. The estimated normal and peak loads for the various departments are given and a suitable power-station design is suggested.

Some Observations on Cut Necks in Rolling Mill Practice. G. P. Contractor and S. Viswanathan. (Sheet Metal Industries, 1946, vol. 23, June, pp. 1087-1096). The causes of scoring and galling on the necks of the rolls of two-high mill stands for finishing sheets are discussed with notes on inverse segregation, structure and composition of the bearings and rolls, and the type of lubricating grease. Micro-examination of nearly 100 bearings did not show that any one structure had a greater tendency to cause cut necks than another. It was noticed that bearings cast from a relatively high temperature (1150° C.) showed more wear than those cast at about 1050° C.

Design and Performance of Plastic Rolling Mill Bearings. O. K. Graef. (Steel, 1946, vol. 118, May

27, pp. 117-120, 138-142). The properties of plastic bearings for rolling mills are considered and some principles to be observed in their application are pointed out. These are: (1) The amount of water required for lubrication is less than 1% of that for cooling; (2) at 100° F. the viscosity of water is too low for good lubrication; (3) the fit of the back of the liner into the chuck is a controlling dimension and must be accurate; and (4) provision must be made for the swelling of plastic bearings in all directions except towards the chuck.

Investigation of Friction and Wear under Quasi-Hydrodynamic Conditions. R. G. Larsen and G. L. Perry. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 45-50). A laboratory study has been made of the factors which influence fracture and wear by mineral oils containing addition agents under conditions between those of hydrodynamic and true boundary lubrication. The concentration of the number of sulphur-phosphorus compounds required for minimum wear varied over a wide range. The minimum effective concentration is determined by the presence in the

molecule of acidic groups which concentrate the addition agent at the wearing surfaces.

Cold Rolling Plant—A Modern Installation in South Wales. (Iron and Steel, 1946, vol. 19, June, pp. 393–394, 396). An illustrated description is given of the cold-rolling mills at the works of the Whitehead Iron & Steel Co., Ltd. The plant now consists of 4-high reversing and tandem mills, with 2-high and 4-high skin-pass mills, having speeds up to 1250 ft./min. The range of products extends up to 21 in. wide, in gauges of 0.004 in. to 0.125 in.

Lukens—Pioneer in Steel Plates and Plate Products. T. J. Ess and T. E. Madsen. (Iron and Steel Engineer, 1946, vol. 23, May, pp. L-17–L-38). A detailed and illustrated description is given of the steel furnaces and rolling mills of the Lukens Steel Company,

Coatesville, Pennsylvania. The plant has twelve open-hearth furnaces and a capacity of 624,000 tons of ingots per annum, and there are two heavy plate mills with rolls 112 in. and 120 in. long respectively.

Large Shipyard Plate-Bending Rolls. (Engineer, 1946, vol. 182, July 5, p. 9). An illustrated description is given of a plate-bending machine designed to cold-bend plates of steel (44 tons/sq. in. tensile strength) up to 40 ft. long and 1½ in. thick.

Roller Levelling Machines for Armour Plate. (Engineering, 1946, vol. 162, July 19, pp. 56–58). A description is given of three roller levelling machines for straightening tank armour plate up to 12 mm. thick by 40 in. wide, up to 20 mm. thick by 60 in. wide, and up to 25 mm. thick by 86 in. wide.

HEAT-TREATMENT

(Continued from pp. 25 A–26 A)

Heat-Treatment of Metals and Alloys. J. W. Donaldson. (Metallurgia, 1946, vol. 34, May, pp. 25–28, 24). The more recent developments and improvements in the industrial heat-treatment of both ferrous and non-ferrous metals and alloys are reviewed.

Some Recent Heat-Treatment Furnace Installations. (Metallurgia, 1946, vol. 34, May, pp. 29–40). Descriptions are given of modern heat-treatment furnaces and equipment, some of which were on the secret list during the 1939–45 period.

Heat Treatment of Stainless Steel. H. Solakian. (Iron Age, 1946, vol. 157, May 30, pp. 46–49). Recommendations are made on the equipment for heat-treating stainless steel. Gas-fired furnaces with alloy-steel containers are recommended for pre-heating and intermediate quenching—operations performed at 1250–1450° F. and 900–1100° F. respectively. For the high-temperature furnace to work at 1650–1950° F., a salt bath heated internally with three electrodes is the most suitable. Data on the rate of preheating and the holding time at high temperature for different thicknesses of stainless steel are presented.

Heat Treatment and Heat Transfer. L. Rotherham. (Metal Treatment, 1946, vol. 13, Summer Issue, pp. 135–140). A simple account is given of the factors involved in heating and cooling masses of steel of different sizes, and of the relations between cooling conditions and the transformations in steel.

Temperature Uniformity in Heat Treatment of Coiled Metal. V. Paschkis. (Wire and Wire Products, 1946, vol. 21, May, pp. 369–374, 407, 408). The conditions which promote the uniform heating of coils of strip and packs of sheets in heat-treatment furnaces are discussed. The transfer of heat to a coil should be in an axial direction and for the best results not more than two coils should be placed one on top of the other.

Application of Controlled Atmospheres to the Processing of Metals. C. E. Peck. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 501–509). A summary is given of the

application of special atmospheres to a wide variety of heat-treating processes. Details of the principal types of atmospheres and the equipment required for preparing them are given.

Gas Carburizing. (Iron and Steel, 1946, vol. 19, June, pp. 387–388). The advantages of controlled gas-carburizing are outlined and a semi-batch-type installation employing town's gas as the source of thermal energy is described.

Gas Carburizing. P. F. Hancock. (Machinery, 1946, vol. 69, July 4, pp. 1–8). The advantages of gas-carburizing and the requirements of carburizing atmospheres are considered, and descriptions are given of modern stationary and rotary-drum types of batch furnaces. Data on the operating costs are presented.

Flame Hardening Cast Iron. R. H. Olmsted. (Foundry, 1946, vol. 74, May, pp. 152–155, 284–286). The flame-hardening of cast iron and its advantages are discussed. When the flame-hardened case ends in an area of tensile stress it is advisable to apply a low-temperature stress-relieving treatment.

Selective Induction Hardening of Previously Hardened Parts. R. C. Gibbons. (Steel, 1946, vol. 118, May 27, pp. 92–93, 134–136). A sequence of processes for the selective hardening of machined parts for aircraft is described. This sequence consists of (1) rough-machining, then quenching and tempering to produce a medium hardness of the core; (2) finish-grinding of areas to be induction-hardened; (3) induction-hardening of specified areas; (4) tempering these areas; and (5) polishing or lightly sand-blasting.

Induction Heating of Hollow Metallic Cylinders. A. Gemant. (Journal of Applied Physics, 1946, vol. 17, Mar., pp. 195–200). The heat input to hollow cylindrical metal cores subjected to induction heating is discussed and an equation is developed for calculating the heat input at any of the frequencies used.

Heat Treatment of High-Speed Steel. M. Cohen and P. Gordon. (Iron Age, 1946, vol. 157, Feb. 28, pp. 42–47; Mar. 7, pp. 52–57; Mar. 14, pp. 68–73; Mar. 21, pp. 61–65; Mar. 28, pp. 55–62). In the first

part of this series of articles the fundamental theory of the heat-treatment of high-speed steel is explained. In Part II. cooling from the austenitizing temperature and the four stages of tempering are dealt with. Part III. is devoted to the effects of tempering time and temperature on secondary hardness, and the kinetics of the tempering process. Parts IV. and V. are concerned with the effects of interrupted cooling after tempering, the effects of treatment at sub-zero temperatures, and of tempering before and after sub-zero cooling.

High-Speed Hardening without Atmospheres. W. B. Macnerland. (Steel, 1946, vol. 118, June 3, pp. 107, 152). A simple method of hardening high-speed steel is described. It consists of preheating the tool to 700–1000° F. and immersing it in a molten boric-acid bath held at the required hardening temperature.

Improving High Speed Steels. (Steel, 1946, vol. 118, June 3, p. 116). There is often some segregated free carbide in a brittle mass near the centre of high-speed

steel bars. An American firm has developed a process called "Desegatizing" by which an almost uniform distribution of the carbides is obtained. Some advantages of the process are outlined.

The Sub-Zero Treatment of High-Speed Steel, with Special Reference to Intermittent Cutting. K. J. B. Wolfe. (Metal Treatment, 1946, vol. 13, Summer Issue, pp. 79–94, 98). The results of tempering at 580° C., sub-zero treatment at –76° C., and combinations of the two on three high-speed steels were studied by micro-examination, hardness tests, and magnetic analysis. The steels were a 6/6 tungsten-molybdenum steel, and 18/4/1 and 22/4/1 tungsten-chromium-vanadium steels, the latter with 10% of cobalt. These steels require two to four temperings at 580° C. to complete the austenite martensite inversion. Treatment at –76° C. produces a similar physical change, but of smaller magnitude than does tempering. Machining tests involving intermittent cutting were also carried out with these three steels.

WELDING AND CUTTING

(Continued from pp. 26 A–28 A)

This Elusive Character Called Weldability. W. L. Warner. (Welding Journal, 1946, vol. 25, Mar., pp. 185-S–188-S). The changes in the significance of the term "weldability" with improvements in welding technique are pointed out and the following definitions of weldability (proposed by the Weldability Committee of the Welding Research Council of the American Welding Society) are analysed and discussed: (a) Weldability of a metal is the capacity of that metal to be fabricated by welding, under the conditions imposed, into a structure adequate for the intended purpose; and (b) weldability of a metal is the capacity of that metal to be fabricated with a prescribed welding procedure without detriment to its required service properties.

Welding. (British Intelligence Objectives Sub-Committee, 1945, Fiat Final Report No. 497: H. M. Stationery Office). An investigation was made to determine the extent of German developments in welding during the war years, and the present report gives the information obtained. In general it was found that Germany is far behind both the United States and Great Britain in the designs of their standard welding machines.

German Welding Rod Manufacture. C. G. Merritt. (Iron Age, 1946, vol. 157, June 6, pp. 66–70). Information on the development and manufacture of welding rods in Germany is presented. The compositions of many German rods and coatings are given.

Rebuilding Locomotive Wheels by Automatic Shielded Arc Methods. L. K. Stringham. (Welding Journal, 1946, vol. 25, Apr., pp. 336–339). Details are given of the welding process developed by an American railway company for building up worn locomotive wheel rims. In this shielded-arc process a stream of crushed manganese-silicate is poured on to the weld; the electrode is fed continuously from a coil of wire and the arc is submerged under the manganese-silicate flux.

Design of Fixtures for Projection Welding. M. L. Ochiano. (Iron Age, 1946, vol. 157, May 2, pp. 55–56). The design of dies and holders for electric projection-welding machines is discussed and examples are illustrated.

Processing and Fabrication of Stainless Steel Sheet and Plate Products. H. S. Schaufus and W. H. Braun. (Steel Processing, 1946, vol. 32, Mar., pp. 164–167; Apr., 234–238, 248; May, pp. 301–305). The equipment and techniques for welding stainless steel by electrical methods, as well as by special methods using atomic hydrogen, argon, and helium, are discussed and data on the properties of some of the welds obtained are presented.

Impact Resistance of Welded Stainless. J. G. Henderson. (Steel, 1946, vol. 118, May 13, pp. 94, 112). Particulars are given of the best welding technique to apply in the welding of stainless steel which is to be used at low temperatures.

Multiple Tip Torches Speed Stainless Steel Welding. W. P. Brotherton. (Iron Age, 1946, vol. 157, June 20, pp. 70–73). Descriptions are given of multiple-tip welding torches for simultaneous welding and cutting, and simultaneous preheating and welding. Other equipment described includes a light-weight atomic-hydrogen welding torch and a simple ball-jointed clamp for holding pieces of irregular shape.

A Method for Welding Sheet Aluminium to S.A.E. 4140 Steel. W. F. Hess and E. F. Nippes, jun. (Welding Journal, 1946, vol. 25, Mar., pp. 129-S–148-S). A study was made of a large number of metals to find one to use as a bond between aluminium and steel to produce a strong joint with high thermal conductivity. The important conclusion reached was that plating a layer of silver of the correct thickness on the steel was the best means of obtaining a good bond when subsequently welding aluminium sheet to the steel. In the second part of the report the hardening of steel S.A.E. 4140 (a chromium-molybdenum steel)

as a result of welding, and the actual seam welding of aluminium fins to steel cylinder barrels are considered.

Some Observations on the Effect of Oxygen on Carbon in Steel. L. Fine and C. H. Maak. (Welding Journal, 1946, vol. 25, May, pp. 283-S-287-S). A drop in hardness has been observed in the weld plane of oxy-acetylene welds in low-alloy medium-carbon steels made under poor welding conditions. Etching has produced evidence of considerable dissolved oxygen in such welds. Experiments to study this phenomenon are reported. It was found that the deliberate introduction of oxygen into the weld caused "auto-decarburization" i.e., the movement of carbon from one internal region to another; the consequent reduction in the carbon content of the weld plane caused a decrease in the hardness.

Flakes in Welds. M. Lefevre. (Revue de la Soudure, 1945, vol. 1, No. 2, pp. 39-49). The appearance and possible causes of flakes and "fish eyes" in steel, and more particularly in welds, are considered, and the results of tests indicating their effect on the properties of the steel are presented. In most cases the flakes disappear after the part has been in service for a short time. They can be got rid of by heating for a few minutes at 400° C. or for a few hours at 250° C.

Factors Affecting Weld Cracking and How to Overcome Such Conditions. L. K. Stringham. (Welding Journal, 1946, vol. 25, May, pp. 440-441). Methods of preventing cracks in fillet welds are described. Slightly convex beads are less apt to crack than flat or concave shapes. A good analysis of steel for high-speed welding without cracks is carbon 0.13-0.20%, manganese 0.40-0.60%, silicon 0.10% max., sulphur 0.035% max., and phosphorus 0.04% max.

The Hard-Zone or Underbead Cracking of Alloy Steels on Welding. G. L. Hopkin. (Metal Treatment, 1946, vol. 13, Summer Issue, pp. 145-150). Recent literature on hardness and crack formation in the heat-affected zone of welds is reviewed.

High-Strength Pressure Welded Joints. C. B. Voldrich and J. L. Zambrow. (Steel, 1946, vol. 118, Apr. 15, pp. 98-99, 136-144). Work at the Battelle Memorial Institute on oxy-acetylene pressure-welded joints in seamless steel tubes $3\frac{1}{8}$ and $3\frac{3}{8}$ in. in outside dia. with walls $\frac{1}{2}$ in. thick, is described, the object being to determine the optimum technique and the effects of changes in pressure, temperature, duration of heating, and sequence of operations.

Castings and Weldings. C. D. Gibb. (Institute of British Foundrymen, 1946, vol. 79, June 20, pp. 179-184, 191; Engineer, 1946, vol. 181, June 28, pp. 591-594). The relative merits of welded and cast construction for housings and components of turbo-alternators and power-generating equipment are pointed out. The necessity of attracting more moulders into the foundry industry is stressed and suggestions for doing this are made.

Industrial Electronics. (Engineer, 1946, vol. 182,

July 19, pp. 54-55). Descriptions are given of electronic apparatus, such as the thyatron voltage regular, which is used to control electrically-driven machines, especially welding machines.

Electric Furnace Copper-Brazing of Steel Parts. H. M. Webber. (Materials and Methods, 1946, vol. 23, Mar., pp. 725-728). A detailed description is given of the brazing of steel parts to make up an incendiary-bomb case. This was done by assembling the parts with copper wire rings close to the joints and passing them through a furnace on a belt conveyor, the temperature being high enough to melt the copper and run it into the joints.

Filler Metal Flow in Brazed Steel Joints. (Iron Age, 1946, vol. 157, Apr. 11, pp. 60-61). An investigation to determine the distance silver-alloy filler metal will flow in relation to joint spacing, type of parent metal, and direction of flow in steel brazing operations is discussed.

Should Steel Parts Cut by Oxy-Acetylene Be Given Supplementary Treatment? G. Ancion. (Revue de la Soudure, 1945, vol. 1, No. 2, pp. 27-38). Tests at the laboratories of the Société Anonyme l'Oxyhydrique Internationale on the condition and properties of the edges of steel plates after oxy-acetylene cutting are described. The results indicated that plates with a tensile strength of up to 55 kg./sq. mm. require cleaning with a wire brush only. Steel of higher tensile strength requires either preheating at 250-400° C. or post-heating to 600-650° C. with slow cooling.

Stack-Cutting Thin Steel Sheets. (Machinery, 1946, vol. 69, July 4, pp. 11-13). A description is given of an automatic oxy-acetylene cutting machine for cutting stacks of thin steel sheets. The movement of the torch head is controlled by a magnetic wheel which is operated in contact with the template.

U.S. Navy Developments in Underwater Cutting. B. Ronay and C. D. Jensen. (Welding Journal, 1946, vol. 25, Mar., pp. 201-209). Methods of cutting metals developed for salvage work by the United States Navy are described in detail. The arc-oxygen technique is used, employing an insulated holder gripping a steel tube electrode, connected to a welding generator and a cylinder of oxygen. The oxygen supply is controlled by a lever in the diver's hand. The diver telephones for the current to be switched on; he strikes an arc with the electrode against the plate to be cut and releases a flow of oxygen which passes down the inside of the electrode. Both the plate and the electrode are burnt away as with an oxygen lance. The outer surface of the electrode is insulated with a waterproof coating which burns away more slowly than the metal tube.

Flame-Cutting Steel under Water. G. V. Slottman. (Machinist, 1946, vol. 90, May 25, pp. 244-247). The difficulties encountered in flame-cutting steel under water are explained and details are given of the equipment and methods which have been devised to overcome them.

MACHINING

(Continued from p. 29 A)

How to Work Stainless Steel. H. L. Flynn. (Machinist, 1946, vol. 90, June 15, pp. 379-398). This article contains information on the latest methods of machining, heat-treating, forging, pickling, welding, riveting, soldering, cold-working, grinding, and polishing stainless steel.

Relation of Surface-Roughness Readings to Actual Surface Profiles. L. P. Tarasov. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 189-194). Studies of surface finish have shown the desirability of relating profilometer-roughness readings to actual peak-to-valley distances of the type that a micrometer measures. Approximate multiplying factors for converting profilometer readings into peak-to-valley roughness have been obtained from taper sections of a variety of abrasive-finished steel surfaces with profilometer roughness in the range of 1 to 100 micro-inches root-mean-square roughness.

Influence of Applying Cutting Fluids at Different Temperatures When Turning Steel. O. W. Boston, W. W. Gilbert, and R. E. McKee. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 217-222). An investigation is described the object of which was to determine the influence on cutting speed, tool life, chip formation, and other factors, of a cutting fluid applied at each of several different constant temperatures ranging from 55° F. to 150° F.

Conference on Surface Finish. (Proceedings of the Institution of Mechanical Engineers, 1945, vol. 153, pp. 331-379). The following papers were presented at the Conference on Surface Finish held at the Institution of Mechanical Engineers on March 9, 1945:

The Structure of Sliding Surfaces, by G. I. Finch.

A Short Review of Surface Finish in Relation to Friction and Lubrication, by D. Clayton.

Some Principles and Methods of Surface Measurement, by R. E. Reason.

Measurement of Surface Waviness, by C. Timms.

Rational Specification of Surface Finish, by W. A. Tuplin.

Requirements in Surface Finish, by D. McConnell.

Surface Finish in Production Methods, by W. E. R. Clay.

Results of Modern Practice, by F. Nourse.

Continuity in the Production of Specified Surface Finish, by E. Swain.

Effect on Fatigue Strength, by W. Ker Wilson.

A Glossmeter for Smoothness Comparisons of Machine-Finished Surfaces. R. S. Hunter. (Journal of the Optical Society of America, 1946, vol. 36, Mar., pp. 178-181). A photoelectric glossmeter has been developed for use in comparing the roughnesses of machined surfaces. Although this instrument actually evaluates that fraction of surface area nearly parallel to the mean surface and not shaded by peaks, the instrument gives rapid and reasonably reliable comparisons of the roughness of different surfaces prepared with about the same tool feeds. Because glossmeter readings depend on the profile shapes rather than profile dimensions, the glossmeter is not a suitable instrument for roughness comparisons where tool feeds differ appreciably from specimen to specimen.

Measurement of Surface Roughness. C. Timms. (Metal Treatment, 1946, vol. 13, Summer Issue, pp. 111-118). This paper was presented at a Congress in Paris organized by La Commission Technique des États et Propriétés de Surface des Métaux. It indicates the progress made in Great Britain on the measurement of surface roughness and describes some of the instruments which have been developed for this purpose. The range of roughness which each type of instrument can accommodate is shown. The progress made in establishing a rational specification for surface roughness is indicated. The unit adopted for the measurement of surface roughness in British practice is the micro-inch (0.000001 in.).

Surface Finish of Reduction Gear Teeth. J. A. Davies. (Journal of the American Society of Naval Engineers, 1946, vol. 58, Feb., pp. 16-20). The "Faxfilms" method of obtaining a reproduction of the surface condition of reduction-gear teeth is briefly described. The films can be mounted, used as a slide, and projected on to a screen or white wall at about 40 magnifications. Several examples of the films showing surfaces finished in different ways are reproduced.

PROPERTIES AND TESTS

(Continued from pp. 31 A-35 A)

Atomic Physics and the Strength of Metals. N. F. Mott. (Journal of the Institute of Metals, 1946, vol. 13, pp. 367-380). An account is given of the main contributions of quantum mechanics to the physics of metals. The limitations of theory in helping the practical man are stressed. Mathematics can be used to test the consequences of a hypothesis, and to help plan a line of fruitful experimental investigation. The methods of theoretical physics are illustrated by a theory of oxidation of metals, and by

some remarks about the dislocation theory of slip. In the theory of oxidation, it is shown that, when a metal with a thin oxide layer is exposed to air, a constant voltage is set up across the layer, and that growth is usually due to the migration of metal ions through it. The rate of migration is in certain circumstances strongly dependent on the field, so that oxidation practically ceases at a certain thickness. Some new points about the dislocation theory of slip are brought forward, in particular a hypothesis as to

the cause of the high ductility of metals, with some remarks on the theory of precipitation-hardening. It is suggested on theoretical grounds that for precipitation-hardening to have its maximum effect, the distance between the precipitates must not be too small. It is also shown that the dependence of yield stress on temperature at low temperatures ought to depend on this distance.

A Study of the Geometry of the Tension-Impact Specimen. N. A. Kahn and E. A. Imbembo. (American Society for Testing Materials, 1946, Preprint No. A2). Test data are presented on the effect of the length/diameter ratio of the specimen on the tension and impact test results, and recommendations are made on the value of this ratio in order to obtain a true measure of the properties of metallic materials.

Structural Changes in the Process of Rupture in Conjunction with the Characteristic Curves for the Material. T. Pöschl. (Metallwirtschaft, 1940, vol. 19, Apr. 26, pp. 331-335). The technique for presenting the properties of a solid by the stress-strain curve in conjunction with several micrographs, each showing the structure at different states of strain, is described. An example which includes 19 micrographs of steel specimens is given.

Mechanical Methods of Testing. N. N. Davidenkov and N. I. Spiridonova. (American Society for Testing Materials, 1946, Preprint No. 27). An account is given of the method which was developed to study the distribution of stress across the neck of specimens which had suffered different degrees of reduction in the tensile test. This was done by measuring the changes in size of the grains in zones from the centre to the circumference of polished sections through the narrowest part.

Yielding and Fracture of Medium-Carbon Steel Under Combined Stress. E. A. Davis. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. A-13-A-24). The results of combined stress tests on a 0.23%-carbon steel are presented. Particular attention is paid to the magnitude and the distribution of the stresses and strains at the instant preceding fracture. The effect of the shape of the test specimen and the isotropy of the material upon the fracture properties were also investigated.

Tension Tests at Constant True Strain Rates. C. W. Macgregor and J. C. Fisher. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. A-217-A-227). Tension tests of the true stress-strain type are reported for which the true strain rate is maintained constant throughout each test. Several metals are investigated under testing temperatures ranging from 183° C. to 665° C. The influence of temperature and strain velocity on the true stress-strain properties is described. A single variable called the velocity-modified temperature is used to represent the combined influences of true strain rate and testing temperature.

The Tensile Properties of Several Special Steels and Certain Other Materials under Pressure. P. W. Bridgman. (Journal of Applied Physics, 1946, vol. 17, Mar., pp. 201-212). Tensile tests were made on

specimens of two series of steels, the specimens being completely surrounded by a fluid in which pressures of up to 30,000 kg./sq. cm. could be maintained. The first series consisted of four stainless steels with up to 18% of chromium and 10% of nickel; the second comprised five carbon steels with hardnesses of 48 to 63 Rockwell C. Necking started at an abnormally high elongation in the stainless steels with 9% and 10% of nickel and they strain-hardened at a very rapid rate. With the second series, the rate of strain-hardening increased and the effect of pressure on ductility decreased with increasing hardness. The steel with a hardness of Rockwell C 63 had a measurable ductility under a pressure of 24,000 kg./sq. cm.

Simple Method of Determining Poisson's Ratio. R. J. Wilkins. (Engineering, 1946, vol. 162, July 19, p. 52). A description is given of a simple apparatus for experimentally determining Poisson's ratio for a metal in the form of a thin-walled vessel.

X-Ray Diffraction Study of Notch-Bend Test. J. T. Norton, D. Rosenthal, and S. B. Maloof. (Welding Journal, 1946, vol. 25, May, pp. 269-S-276-S). The part played by the notch in notch-bend tests on mild steel plate was studied by X-ray diffraction and by brittle lacquer coatings. It was demonstrated that the notch had no effect on the initiation of plastic flow and, on the other hand, that plastic flow had a marked effect on the stress concentration factor.

Toughness and Fracture of Hardened Steels. M. A. Grossmann. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 2020: Metals Technology, 1946, vol. 13, Apr.). Experiments and metallographic investigations concerning the changes in toughness of hardened and tempered steel are described. From the observations made the following general picture is arrived at: The quenched steel, before tempering, has a high yield strength, so that when the notched bar is stressed beyond the yield strength it very soon reaches the cohesive strength and the piece is brittle; when it is tempered lightly at up to 400° F., the yield strength becomes lower, whereas the cohesive strength falls but little, if at all. Consequently, when the metal is stressed beyond the yield strength, it deforms somewhat more before reaching the cohesive strength, and it is therefore a little tougher than before tempering. Upon raising the tempering temperature from 400° to 500° F., the cohesive strength falls more rapidly than the yield strength, so that there is less deformation and the steel is less tough. On increasing the tempering temperature beyond 500° F. the yield strength falls the more rapidly so that the steel becomes tougher.

Effect of "Fisheyes" on Impact Strength of High-Tensile Manganese-Titanium Steel Plate. M. R. Gross, W. R. Angell, and G. D. Marshall, jun. (Metal Progress, 1946, vol. 49, June, pp. 1173-1180). An account is given of an investigation of the effect of "fish-eyes" on the properties of manganese-titanium steel plate and of the improvement in the properties with ageing. Artificial ageing by heating to 400° F. or natural ageing for one month at room temperature

greatly improves the properties of this steel. The improvement in ductility with ageing is associated with the removal of dissolved or occluded hydrogen from the steel.

A Graphical Method for the Evaluation of Principal Strains from Normal Strains. G. Murphy. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. A-209-A-210). Graphical methods are available for determining principal strains when observed strains are measured along gauge lines which make angles of 45° or 60° with each other. In this paper the author presents a simplified graphical method for the general case in which angles between the gauge lines may have any arbitrary value.

A Graphic Resolution of Strain. N. J. Hoff. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. A-211-A-216). A purely graphical procedure is developed for the resolution of strain data obtained from measurements by strain rosettes of any shape.

Studies of Plastic Flow in Steel, Especially in Two-Dimensional Compression. P. W. Bridgman. (Journal of Applied Physics, 1946, vol. 17, Apr., pp. 225-243). The experimental methods are described by which rectangular blocks are subjected to two-dimensional compressional stresses and at the same time flow is maintained two-dimensionally with deviations of less than 1%. Within this range of flow a rather wide range of stress conditions is possible, so that the equations of plastic flow can be examined over a correspondingly wide range of conditions. By proper lubrication it is, however, possible to produce approximately homogeneous deformations in two-dimensional compression at least up to reductions to two-thirds of the initial length. The time rate of primary flow is studied at various points on the strain-hardening curve. The rate of flow rises rapidly as the stress increases above the limiting strain-hardening curve. The rate of increase of the rate of flow for a given displacement from the limiting curve is much greater in the early stages of flow. It is this which makes possible the calculation of the rate of propagation of a plastic disturbance from the parameters of the static strain-hardening curve. Beyond the early stages of flow new time effects begin to appear. The flow loses its smoothness and becomes more and more inclined to be jerky. At high strains, flow may not start at once when the load is increased, but there may be an initiation period during which flow is built up. The application of the results to the generalized strain-hardening curve is discussed.

The Maybach Stress-Line Process and Its Application to Metals. O. Dietrich. (Metallwirtschaft, 1940, vol. 19, Apr. 26, pp. 337-342). A description is given of the Maybach process of using brittle lacquer coatings to study stress distribution. In this, the lacquer cracks at a stress below the elastic limit of the metal being tested. Examples of its application in the study of stress patterns in an automobile frame, in square and round bars, and in notched bars are given with numerous illustrations.

Neumann Bands and the Planar-Pressure Theory of Hydrogen Embrittlement. C. A. Zapffe. (Iron and

Steel Institute, 1946, this Journal, Section I). In a broad review of published work on Neumann bands, reason is found for disbelieving the present accepted theory that these bands represent primarily a twinning phenomenon. A study of Neumann bands in ingot iron and in silicon ferrite with the new micrographic technique known as fractography confirms this doubt. A new theory is offered based upon the rôle of visible planar imperfections seen in fractographs. To test the theory, the passage of hydrogen gas through these irons is studied both before and after deformation by observing the effusion of the gas under oil. The observations provide proof that not only Neumann bands but also slip lines are based on and located by a pre-existent "planar imperfection structure" which must hereafter be considered in all studies of mechanical deformation, and also chemical precipitation. The sudden appearance of the hydrogen bubble, its constant size, and the confinement of its appearance to bands and slip markings, simultaneously afford proof for the fissured structure of these bands and for the planar-pressure theory of hydrogen embrittlement advanced earlier by the author. The conclusion is drawn that deformation bands in general comprise primarily a shearing movement of adjoining mosaic sections, and that the material within the zone of shear has a mathematical probability for twinning which varies from approximately 1.0 in metals such as bismuth and zinc to virtually 0.0 for certain other metals. In spite of the unlikelihood of twinning in body-centred-cubic structures, α -iron is known definitely to twin under certain conditions. Hence Neumann bands may be twinned or they may not, their condition with respect to twinning not being fundamental to an understanding of the band phenomenon.

Graphitization of Low-Carbon and Low-Carbon-Molybdenum Steels. H. J. Kerr and F. Eberle. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, Graphitization of Steel Piping, pp. 1-35). The service behaviour of steel tubes and the results of laboratory tests on graphitization led to the following conclusions: (1) Low-carbon steel with an abnormal structure after ordinary heat-treatment graphitized in a random arrangement in the observed temperature range of 850 – 1020° F. with reasonable stress; (2) Low-carbon steel with a normal structure, under identical conditions for $8\frac{3}{4}$ years at 1020° F., was found to be free from graphite in zones affected and unaffected by the heat of welding. (3) Welded steel with an abnormal structure showed no more graphitization in the heat-affected zone than in the unaffected zone. (4) Some medium-carbon steels graphitized and others did not. The following conclusions refer to low-carbon/molybdenum steel: (5) These steels with either normal or abnormal structures showed slight, if any, graphite after $5\frac{1}{2}$ years' service at 935 – 950° F., or after 4 years at 1050° F., except in cases where the abnormal steel has been subjected to heating and cooling through the lower critical range; this indicates that molybdenum increases the resistance to graphitization. (6) Increased rates of heating and cooling favour the formation of graphite. (7) The molybdenum steel with

a normal structure, when subjected to heating cycles in the laboratory, did not develop graphite after 6000 hr. at 1000° F.; and (8) the McQuaid-Ehn test was valuable in determining the graphitizing tendency of carbon and carbon-molybdenum steels.

Progress Report on Graphitization of Steam Lines. S. L. Hoyt and R. D. Williams. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, Graphitization of Steel Piping, pp. 47-55). Since the discovery of segregated graphite alongside a welded joint in carbon-molybdenum steel steam pipe at a power station in 1943, other power stations have investigated the condition of their own steam pipes. This paper reports certain aspects of the work done, the progress to date being outlined. The renovation of lines in which graphite is forming, the deoxidation practice and the best composition to prevent graphitization, and welding are all given close attention. After 1500 hr., very considerable amounts of graphite were present in many of the plain carbon steels tested, whereas in the comparable group of molybdenum steels, small amounts of graphite were found in the high-aluminium deoxidised type only.

Investigation of Graphitization at Detroit. R. M. Van Duzer, jun., I. A. Rohrig, and A. McCutchan. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, Graphitization of Steel Piping, pp. 57-63). An investigation of deterioration of welded joints in steam pipes at a Detroit power-station is reported. No serious case of graphitization was discovered. Dispersed graphite was found in some cases. Laboratory tests for 3300 hr. at 1000-1060° F. confirmed the evidence obtained from pipe joints in service that carbon-molybdenum steel pipes low in aluminium have greater resistance to graphitization than steel high in aluminium.

A Study of Austenitic Welding for Control of Graphitization in Steel. I. A. Rohrig. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, Graphitization of Steel Piping, pp. 65-73). See p. 10 A.

Graphitization of Carbon-Molybdenum Steel in High-Temperature Steam Piping. G. A. Timmons. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, Graphitization of Steel Piping, pp. 77-82). See Journ. I. and S.I., 1946, No. I., p. 69 A.

Graphitization of Welded and of End-Quenched Carbon and Molybdenum Steels. G. V. Smith and S. H. Brambir. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, Graphitization of Steel Piping, pp. 85-89). End-quenched specimens and welded samples of a series of carbon steels (with from 0.15% to 0.80% of carbon) and of low-carbon 0.5%-molybdenum steels were examined for graphite after 1000, 2000 and 3000 hr. at 975-1050° F. Some of these were heat-treated for 4 hr. at 1300° F. immediately after welding to prevent graphitization. Local graphitization occurred in the heat-affected zone of a rapidly-deposited weld on molybdenum steel; this graphitization was prevented if the specimen was heated for 4 hr. at 1300° F. No graphite was found in end-quenched specimens of molybdenum steel, but all the end-quenched carbon

steels graphitized, and, of the structures present in these specimens, martensite was most subject to graphitization, the number of nodules being large and their size small. In the pearlite region, on the other hand, the number of nodules was very small and their size relatively large.

Graphitization in Some Cast Steels. A. J. Smith, J. Urban, and J. W. Bolton. (American Society of Mechanical Engineers: Welding Journal, 1946, vol. 25, May, pp. 257-S-268-S). An account is given of laboratory studies of graphite formation in cast steel as well as a report on the condition of castings used in high-temperature steam plant. The prevention of graphitization does not seem possible by controlled melting or deoxidation practice, or by heat-treatment. Protection should be sought by employing weak carbide-forming elements in conjunction with the strong carbide-forming element molybdenum so as to decrease the proportion of molybdenum dissolved in the ferrite and increase the amount available to form the very stable molybdenum carbide. The addition of elements having a stronger affinity than molybdenum for carbon would force more molybdenum into the ferrite, leaving these added elements to form the principal carbides.

Influence of Heat Treatment upon the Susceptibility to Graphitization of High Aluminium Deoxidized Carbon-Molybdenum Steel. F. Eberle. (American Society of Mechanical Engineers: Welding Journal, 1946, vol. 25, May, pp. 307-S-312-S). The effect of heat-treatment on the graphitization of low-carbon 0.5%-molybdenum steel was investigated. A study of the test data led to the following conclusions: (1) Annealing at a very high temperature followed by rapid cooling seems to inhibit or retard graphitization; this was found to be true also for specimens which had been cold-reduced 50% by compression before sub-critical annealing at 1000° F. (2) Annealing at temperatures above, but near to, the A_3 point of the steel followed by rapid cooling appears to be much less effective in retarding graphitization than rapid cooling from a very high temperature; when severely cold-deformed, such material may form graphite within 1500 to 3000 hr. at 1000° F. (3) Annealing at temperatures above, but close to, the A_3 point followed by slow cooling renders the steel less susceptible to graphitization than slow cooling from a very high temperature, but more susceptible than cooling in air from temperatures above, but close to, the A_3 point. (4) Reheating steel which had been rapidly cooled from a very high temperature (thereby made resistant to graphitization) to temperatures just above the A_1 point renders it again susceptible, irrespective of the subsequent rate of cooling. (5) Heating to just above the A_1 point (1400° F.) followed by quenching in water renders the steel more susceptible to graphitization than slow cooling in the furnace from the same temperature. (6) Long-time annealing at 1300° F. considerably retards the formation of graphite and also tends to reduce the number of nodules formed.

The Effect of Carbide Spheroidization upon the Rupture Strength and Elongation of Carbon-Molybdenum Steel. G. H. Weaver. (American Society for

Testing Materials, 1946, Preprint No. 55). Specimens from a plate of 0.42% molybdenum steel were treated to obtain twelve different conditions by varying the heat-treatment and the amount of spheroidization. They were then subjected to long-time rupture and elongation tests at 900° and 1000° F. The following conclusions were reached: (1) There was a tendency for the steel to have a common rupture stress irrespective of the heat-treatment; (2) the elongations at rupture for all conditions of the steel, except those with initially spheroidized carbides, decreased rapidly with time; and (3) it is not safe to extrapolate the rupture stress and elongation data from 10,000 hr. to 100,000 hr.

This investigation is a continuation of one reported previously (see Journ. I. and S.I., 1942, No. I., p. 244 A).

Carbon Absorption of 18-8 Stainless Steel. W. G. Hubbell. (Iron Age, 1946, vol. 157, June 13, pp. 56-59). An investigation is reported the object of which was to determine whether aero-engine exhaust manifolds of stainless steel picked up carbon from the hot exhaust gases. In the manifolds examined there was an increase in the carbon of from 0.023% to 0.06% which contributed to the formation of a heavy network of carbides. The corrosion resistance was not materially reduced by the increase in carbon.

Recent Developments in Materials for Gas Turbines. T. A. Taylor. (Proceedings of the Institution of Mechanical Engineers, 1945, vol. 153, pp. 505-512). An attempt is made to describe the recent developments which have taken place in materials appertaining to gas turbines and their effect on general engine development, as well as to describe some of the failures experienced and the methods used in overcoming them.

Carl Schenk Torsion Bar Testing Machine. (British Intelligence Objectives Sub-Committee, 1945, Fiat Final Report No. 402: H.M. Stationery Office). A description is given of a torsion-fatigue testing machine made by Carl Schenk G.m.b.H., which is capable of testing bars up to 79 in. long and exerting a torsional moment of plus or minus 21,500 ft. lb.

On Fatigue Failure Under Triaxial Static and Fluctuating Stresses and a Statistical Explanation of Size Effect. F. H. Fowler, jun. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 213-215). The framework for establishing a criterion of safe fatigue characteristics of manufactured units is developed; in addition, a statistical theory of fatigue is indicated.

Fatigue Strength of $5\frac{1}{4}$ in. Diam. Shafts as Related to Design of Large Parts. O. J. Horger, T. V. Buckwalter, and H. R. Neifert. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. A-149-A-155). This paper reports the results of rotating-cantilever combined-fatigue tests made on shafts of a 0.52%-carbon steel having different size fillets connecting one portion $5\frac{1}{4}$ in. in dia. to another portion $6\frac{9}{16}$ in. in dia. The radii of the polished fillets varied from $\frac{9}{32}$ in. to $\frac{27}{32}$ in., and these were tested to determine the permissible design fatigue strength on the basis of 30,000,000 revolutions. Seven shafts having $\frac{9}{32}$ -in. fillets rolled with a single-

roller burnishing tool were also tested. A comparison is also made between the results obtained by other investigators on small specimens with those now reported on larger members.

Fatigue Testing of Roller Bearings. H. R. Gibbons. (American Society for Testing Materials, 1946, Preprint No. 46). An account is given of the methods and machines used for testing roller bearings and determining their load ratings.

Cumulative Damage in Fatigue. M. A. Miner. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. A-159-A-164). The theory is advanced that cumulative damage under repeated loads is related to the net amount of work absorbed by the specimen; this means that the number of load cycles expressed as a percentage of the number to failure at a given level of stress represents the proportion of useful life expended. Tests with an aluminium alloy supported the above theory and further tests with steel are advocated.

A Study of the Damaging Effect of Fatigue Stressing on X4130 Steel. J. A. Bennett. (American Society for Testing Materials, 1946, Preprint No. 33). The damaging effect of fatigue-stressing notched specimens of a chromium-molybdenum steel at above the endurance limit was investigated; this was measured by the decrease in endurance at another stress. A deflection method for detecting the formation of a fatigue crack permitted the damage measurement to be limited chiefly to the pre-crack stage. The results showed that the apparent rate of damage depends on the stress history. If the pre-stress is higher than the test stress the damage occurs rapidly at first, then more slowly. The reverse is true if the damaging stress is lower than that used to measure the damage.

Automotive Rear Axles and Means of Improving Their Fatigue Resistance. O. J. Horger and C. H. Lipson. (American Society for Testing Materials, 1946, Preprint No. 29). The effects of cold-straightening, three degrees of shot-peening, and recarburization on the fatigue strength of low-alloy chromium-nickel steel axle shafts for automobiles were investigated. The endurance limit of unstraightened axles was about 25% higher than that of straightened ones. The endurance limit of shot-peened straightened axles was about three times that of straightened axles not shot-peened. If carburized shafts were accidentally decarburized during heat-treatment their fatigue resistance was lowered.

Fatigue Tests of Rail Steel under Compressive Stress. R. S. Jensen and H. F. Moore. (American Society for Testing Materials, 1946, Preprint No. 38). The results are reported of fatigue tests on rail steel in which the range of stress varied from a maximum compressive stress to a tensile stress 20% of the value of the former. In all the specimens tested the fatigue crack started on the compression side of the specimen. Stamping a number on the critical section of the surface of the specimen in compression caused a marked reduction in the fatigue strength. Shot-peening the specimens raised the fatigue strength 32% above that of specimens in the as-rolled condition.

Fatigue Testing Machines for Ball and Roller Bearings. T. Barish. (American Society for Testing

Materials, 1946, Preprint No. 42). Fatigue testing machines for ball and roller bearings are described and some of the results obtained with them are presented.

Metallographic Observations of Ball Bearing Fatigue Phenomena. A. B. Jones. (American Society for Testing Materials, 1946, Preprint No. 45). The fatigue characteristics of a 1%-carbon 1.20-1.50%-chromium ball-bearing steel were investigated by studying micrographs.

Extending the Jominy Scale. J. Erb. (Iron Age, 1946, vol. 157, June 13, pp. 48-51). A simplified method for estimating the hardness of quenched and tempered steel from hardenability data is described.

A Thermal-Balance Method and Mechanical Investigation for Evaluating Machinability. A. O. Schmidt, W. W. Gilbert, and O. W. Boston. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 225-232). The first part of this paper reports the results of an investigation of a calorimetric process for the determination of drilling forces. The second part gives a description of the machine used and the tests made before the investigation with the calorimetric apparatus.

Metallurgical Aspects of Machinability. F. J. Robbins. (Iron Age, 1946, vol. 157, Mar. 21, pp. 42-47; Mar. 28, pp. 47-51). The effects of varying amounts of carbon, sulphur, manganese, lead, and sodium bisulphite in steels are discussed with particular relation to their influence on microstructure and consequently upon machinability. Special emphasis is given to the question of spheroidization in alloy steels, and the effects of grain-size, resulphurization, and addition of sodium bisulphite are considered.

Hypersonic Non-Destructive Testing of Material. (Steel Processing, 1946, vol. 32, Mar., pp. 171-173). A brief description is given of an apparatus for the non-destructive testing of materials by transmitting waves at supersonic frequency through it and picking up the wave pattern with a receiving element on the opposite side.

A Method for Predicting Failure of Metals. P. E. Cavanagh. (American Society for Testing Materials, 1946, Preprint No. 23). The possibilities of using changes in high-frequency magnetic and eddy-current losses to predict the failure of metals is discussed and a method of recording these losses is described. The method can be applied to detect the beginning of plastic deformation caused by overloading or fatigue.

Magnetism and the Testing of Materials. R. V. Baud. (Schweizerische technische Zeitschrift: Engineering, 1946, vol. 162, July 12, pp. 41-42). The units by which magnetism and its effects are measured are explained and the theory of the detection of cracks and inclusions by determining the position and magnitude of leakage flux is discussed.

The Magneto-Resistance of High Coercivity Alloys. L. F. Bates. (Proceedings of the Physical Society, 1946, vol. 58, Part 2, Mar. 1, pp. 153-164). Measurements have been made of the change of resistance of ferromagnetic alloys of high coercivity when exposed to longitudinal and transverse magnetic fields. The changes in the cases of the permanent-magnet materials Alni, Alnico (cast and sintered) and Alcomax

II. are in marked contrast to those of pure ferromagnetic metals. The results are discussed on the basis of the domain concept in ferromagnetism.

Determining the Magnetic Permeability from Resistance Measurements of Iron Wires of Different Structures at Frequencies of the Order of 10^8 Hertz in Conjunction with the Magnitude of the Weiss Elementary Domains. M. J. O. Strutt and K. S. Knol. (Physica, 1940, vol. 7, July, pp. 635-654; Laboratoria N.V. Philips' Gloeilampenfabrieken, Separaat 1512). It is shown that the permeability of iron wires at very high frequencies may be determined from the ratio of A.C. resistance to D.C. resistance under certain assumptions. Measurements for this ratio are given for frequencies up to about $3 \cdot 10^8$ cycles/sec. Whereas the permeability, calculated from the above ratio, remains practically constant up to the said frequency at room temperature, it shows a marked decrease with increasing frequency in liquid oxygen for all the measured wires. Reasons for this are discussed.

Magnetic Spectra of Diverse Materials at Various Frequencies. V. Arkadiev. (Journal of Physics, 1945, vol. 9, No. 5, pp. 373-378). A practical method for the elimination of the influence of eddy current on the magnetic permeability of ferromagnetic bodies is pointed out. By this method a true value of the complex magnetic permeability $\mu - i\mu'$ is obtained. By establishing their dependence upon the frequency the magnetic spectra of different substances are found.

New Machines for Creep and Creep-Rupture Tests. M. J. Manjoine. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 111-116). Two new creep-testing machines are described. One combines eight conventional lever-arm creep machines into a single unit, but it has individual furnace controls and recording equipment. The second is a screw-driven creep-testing machine in which the specimen is loaded through a stiff spring; a continuous elongation-time curve up to rupture is automatically recorded without requiring an extensometer on the specimen.

The Diffusion of Gases through Metals. J. D. Fast. (Chemisch Weekblad, 1941, vol. 38, Jan. 4, pp. 2-8; Jan. 11, pp. 19-23; Laboratoria N. V. Philips' Gloeilampenfabrieken, Separaat 1528). (In Dutch).

Boron Treated Steels. R. A. Grange and T. M. Garvey. (American Society for Metals: Steel, 1946, vol. 118, June 10, pp. 98-104). The hardening properties of four grades of carbon steels with and without additions of boron were compared. The steels contained 0.40%, 0.52%, 0.63%, and 0.75% of carbon respectively. The increase in hardenability obtained by additions of up to 0.001% of boron was greatest with the 0.40%-carbon steel and least with the 0.75%-carbon steel. Increasing the boron above 0.001% did not cause any further increase in hardenability.

Hardenability Effects in Relation to the Percentage of Martensite. J. M. Hodge and M. A. Orehoski. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1994: Metals Technology, 1946, vol. 13, Apr.). The effects of manganese, silicon, nickel, and molybdenum on hardenability were studied by the metallographic

examination of specimens heat-treated to 99.9%, 95% and 50% of martensite. It was found that the hardenability effects of these alloying elements decreased in the following order: Molybdenum, silicon, manganese, and nickel.

Iron-Nickel-Cobalt Alloy for Sealing to Glass. G. D. Redston and J. E. Stanworth. (Journal of Scientific Instruments, 1946, vol. 23, Mar., pp. 53-57). This report summarizes work on British-made iron-nickel-cobalt alloys of the Kovar type, intended for sealing to borosilicate glasses. Several measured expansion curves are given for these alloys.

Why Tool Steels Do Not Act Alike. S. C. Spalding. (Machinist, 1946, vol. 90, June 22, pp. 439-444). Tool steels are classified into five groups as follows: (1) Carbon tool steels; (2) alloy tool steels; (3) high-carbon, high-chromium, and air-hardening die steels; (4) hot-work steels; and (5) high-speed steels. The characteristics of these groups are described and the effects of alloying elements are discussed.

Gas Turbines—Work on Flash Butt-Welded Discs and Shafts. D. A. Oliver and G. T. Harris. (Iron and Steel, 1946, vol. 19, June, pp. 379-381, 400). An account is given of the development of Jessop G.18B steel and the method of butt-welding used for making a gas-turbine disc and stub shaft for the Rolls Royce "Weland" engine. The steel in question, which is now almost universally used throughout the whole range of British jet engines and gas turbines, contains carbon 0.4%, manganese 0.8%, silicon 1%, nickel 13%,

chromium 13%, tungsten 2.5%, molybdenum 2%, niobium + tantalum 3%, and cobalt 10%.

Pre-Stressing Rotating Disks. H. Dobkin. (Steel, 1946, vol. 118, June 3, pp. 104-106, 150). A method of testing forged turbine and compressor rotors is described. It consists of running the rotors for 5 to 10 min. at 10-20% above the highest speed at which they will ever be required to operate in an engine. This is done in a heavily constructed evacuated chamber by means of a high-speed air turbine.

English Steels and Their American Equivalents. T. W. Gorgon. (Machinery, 1946, vol. 69, July 4, pp. 17-20). Tables are presented showing the analyses, heat-treatments, and mechanical properties of the English "En" steels and their American equivalents.

En Steels—Some Wartime Experiences. E. Wood. (Iron and Steel, 1946, vol. 19, June, pp. 367-372). The author describes experiences, chiefly during the war, which were met with in a serious attempt to make as wide and positive use as possible of the "En" steels covered by War Emergency British Standard Schedule 970, 1942.

Steel Fishbolts and Nuts for Railway Rails. (British Standards Institution, 1946, No. 64). The standard specification issued in 1913 for railway fishbolts and nuts is brought up-to-date by this publication.

Pressed Steel Gutters, Pipes, Fittings and Accessories. (British Standards Institution, 1946, No. 1091).

METALLOGRAPHY AND CONSTITUTION

(Continued from pp. 35 A-37 A)

The Swedish Electron Microscope. A. Bergqvist. (Teknisk Tidskrift, 1946, vol. 76, June 29, pp. 649-655). (In Swedish). The principles of the electron microscope are explained and a description is given of the instrument designed by M. Siegbahn now being constructed in Stockholm.

X-Ray Checks Casting Quality. (Foundry, 1946, vol. 74, June, pp. 94-95, 262). A description is given of the million-volt X-ray installation for examining castings at the steel foundry of the Bethlehem Steel Company.

Two-Million Volt Industrial Radiography. L. Cardenas. (Iron Age, 1946, vol. 157, June 13, pp. 52-55). The first 2,000,000-V. X-ray unit to be installed in an industrial plant in the United States is described and examples of its use for examining steel castings are discussed.

The Non-Destructive Testing of Materials and X-Ray Protection Methods. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 203: H.M. Stationery Office). A report is presented on the organization and work of the Reichs-Röntgenstelle, Berlin.

The K.W.I. für Eisenforschung, Düsseldorf. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 205: H.M. Stationery Office). The technique developed at the Kaiser Wilhelm Institut für Eisenforschung for the X-ray measurement of stresses is described.

"Forced Secondary" Recrystallization in an Iron-Nickel Alloy. H. G. Müller. (Metallwirtschaft, 1940, vol. 19, June 21, pp. 509-510). It was found that, after annealing a 90%-cold-reduced iron-nickel alloy containing 50% of nickel, there was "forced secondary" coarse recrystallization present in addition to the well-known free secondary recrystallization. This coarse structure was close to the sheared edge of the alloy and its presence had a detrimental effect on the magnetic properties. Additional cold-rolling after shearing and before annealing broke down this structure.

The Vapour Phases of Metals. R. C. Vickery. (Metallurgia, 1946, vol. 34, May, pp. 4-7). The literature and some of the patents on the industrial utilization of differences in the vapour pressures of metals are briefly reviewed with the object of adding to the literary foundation on which further research on metal vapours may be based.

A Review of the Steel Standardization Group's Method for the Determination of Critical Points of Steel. (Metal Progress, 1946, vol. 49, June, pp. 1169-1171). The dilatometric method of determining transformation points advocated by the Steel Standardization Group in 1942 (see Journ. I. and S.I., 1942, No. II., p. 222 A) is reviewed. The Group still believe in the superiority of the dilatometric method, but in the meantime a revised

procedure has been developed, details of which are given.

The Composite Carbides in Steel Cutting Cemented Carbides. A. G. Metcalfe. (Metal Treatment, 1946, vol. 13, Summer Issue, pp. 127-133). The rôle of titanium carbide in helping to form a tenacious oxide

coating on a tool tip, which enhances tool life, is discussed. The author investigated the structure of the titanium and tungsten carbides, and is of the opinion that no compounds are formed in the TiC-WC system, which is a simple solid solution.

CORROSION OF IRON AND STEEL

(Continued from pp. 37 A-39 A)

Corrosion of Stainless Steel Sheet in Marine Atmospheres. (National Bureau of Standards Technical News Bulletin, 1946, Apr., No. 348, pp. 28-29). The results of corrosion tests on stainless steel sheet 0.018 in. thick exposed to marine atmospheres and in the sea are reported. The rate of attack was greatest during the first six months. After three years of exposure most of the specimens failed in fatigue tests at 78-85% of their initial endurance limits. Steels containing 2.5-3.5% of molybdenum were much less susceptible to attack than those containing titanium, columbium or no stabilizing elements.

The Relationship between Welding and the Corrosion of the So-Called Stainless Steels. A. De Sy. (Revue de la Soudure, 1945, vol. 1, No. 2, pp. 3-26). The welding and the corrosion of martensitic and of ferritic chromium steels as well as of austenitic chromium-nickel steels are discussed, and tests are described which show that welding reduces the corrosion resistance of these steels.

Report of Committee A-5 on Corrosion of Iron and Steel. (American Society for Testing Materials, 1946, Preprint No. 3). This report gives a brief account of the work done in the year 1945-46 by the A.S.T.M. Committee A-5 on Corrosion of Iron and Steel, and by the following sub-committees: No. III. on Inspection of Annapolis Tests; No. V. on Total Immersion Tests; No. VI. on Specifications for Metallic-Coated Products; No. VII. on Methods of Testing; and No. VIII. on Field Tests of Metallic Coatings.

Report on Passivation of Corrosion-Resistant Steels. F. L. LaQue. (American Society for Testing Materials, 1946, Preprint No. 5, pp. 5-8). To assist one of the American arsenals in its consideration of specifications for corrosion-resistant steels a questionnaire on passivation treatments and their effects was drawn up and sent to members of the A.S.T.M. Committee A-10 on Iron-Chromium, Iron-Chromium-Nickel and Related Alloys. The questions and answers are given in the present report.

Atmospheric Corrosion Tests on High-Chromium Steels. W. O. Binder and C. M. Brown. (American Society for Testing Materials, 1946, Preprint No. 47). The results are presented of loss-in-weight corrosion tests on specimens of low-carbon steel with chromium contents increasing from nil to 18% which were exposed near Niagara Falls. The rate of improvement in the corrosion resistance with increasing chromium was greatest in the 0-3%-chromium range; the improvement was then less rapid in the 3-12%-

chromium range, and above 12% scarcely any further improvement was reported.

Corrosion-Resistant Steel for Architectural and Structural Applications. H. A. Grove. (American Society for Testing Materials, 1946, Preprint No. 48). A report is presented on the inspection in 1944 of stainless steel parts of buildings in New York, Philadelphia, and Atlantic City, as well as of an express train constructed of corrosion-resistant steel, by a special committee studying the corrosion.

Atmospheric Corrosion Tests of Corrosion-Resistant Steel Wires. A. P. Jahn. (American Society for Testing Materials, 1946, Preprint No. 49). The results are presented of corrosion tests in which bare steel wire and zinc-coated, lead-coated, and copper-coated steel wires were exposed for up to nine years in industrial, coastal, and rural atmospheres.

Weathering Behavior of Corrosion-Resistant Steel Insect Screens. W. A. Wesley and H. R. Copson. (American Society for Testing Materials, 1946, Preprint No. 52). The results of several series of atmospheric corrosion tests are presented. In these tests woven wire-cloth screens of bronze, 18/8 stainless steel, and chromium-nickel-molybdenum steel were exposed in sulphurous, industrial, marine, and rural atmospheres.

Results of 15 Years' Exposure Tests on Corrosion-Resistant Steels. I. V. Williams and K. G. Compton. (American Society for Testing Materials, 1946, Preprint No. 53). The results of exposure tests on ten corrosion-resistant steels in the atmosphere of New York City for 15 years are presented and discussed. The 13%-chromium steels had considerable surface rust, whereas the 17%-chromium steels and the 18/8 stainless steels had rusted slightly.

Corrosion in Crevices. E. H. Wyche, L. R. Voigt, and F. L. LaQue. (Electrochemical Society, Apr., 1946, Preprint No. 23). The nature of corrosion in crevices and its occurrence are described, and seawater tests on various crevice-sealing compounds are reviewed.

Acidic Atmosphere Evaluation of Cleaning on the Corrosion of Steel. C. W. Smith. (Electrochemical Society, Apr., 1946, Preprint No. 25). The effect of different cleaning methods on the corrosion resistance of steel surfaces indoors in industrial atmospheres is dealt with. The "acid atmosphere cell" is described; this was devised as a simple accelerated form of corrosion test to simulate workshop conditions. Its application to evaluate the effect of different cleaning materials is discussed.

Sodium Hexametaphosphate as a Corrosion Inhibitor

for **Ottawa Tap Water**. M. Cohen. (Electrochemical Society, Apr., 1946, Preprint No. 17).

Silica Deposition in Steam Turbines. F. G. Straub and H. A. Grabowski. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 309-314). Laboratory and power-plant tests have been conducted to determine the cause of silica deposition in steam turbines. The tests indicate that the silica leaves the boiler as vaporized silicic acid which later crystallizes on the blades in the lower-pressure stages of the turbine.

History of Potassium Boiler-Water Treatment at Springdale. L. E. Hankison and M. D. Baker. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 317-321). Details are given of the results of two years experience of the treatment of boiler water at a power station of the West Penn Power Company with potassium compounds, which were substituted for sodium salts for conditioning the water of both the high- and low-pressure boilers.

Experience With Potassium Treatment at Windsor Station. W. L. Webb. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 325-328). A comparison is made between the treatments with sodium and potassium to prevent the corrosion of boiler tubes at a power station in the United States. The test has been in progress only seven months, during which no failures occurred in tube walls. The potassium treatment does not prevent the failure of tube walls on which analcite has already been deposited. The rates of accumulation of deposits in the low-pressure turbines receiving steam from the boilers were substantially the same with both treatments.

Embrittlement Cracking in Waters Containing Potassium Salts. A. A. Berk and N. E. Rogers.

(Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 329-333). The manner in which boiler water containing potassium hydroxide increased the embrittlement of boiler steel was investigated, and it was found that potassium-hydroxide solutions could cause intercrystalline cracking of stressed steel. At 250° C. a small concentration of silica in the solutions greatly accelerated the attack. Potassium nitrate and quebracho extract both proved to be quite effective inhibitors.

Experience With Sodium and Potassium Chemicals for Boiler-Water Conditioning at Montaup Electric. G. U. Parks. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 335-338). An account is given of the satisfactory results obtained by changing from all sodium to all potassium treatment of the boiler-water for the high-pressure forced-circulation boiler at the Somerset Power Station of the Montaup Electric Company.

Cavitation in Centrifugal Pumps. A. J. Stepanoff. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. 539-552). A comprehensive survey of the literature on cavitation in centrifugal pumps and turbine rotors is presented and a method for determining the cavitation conditions in relation to velocity is explained. An original explanation is offered of the nature of local high-destructive pressures during cavitation and in cases of metal failure by fatigue in the presence of liquids.

Stress Corrosion Cracking of Mild Steel. Part VII. Preventive Treatments. R. D. Misch, J. T. Waber, and H. J. McDonald. (Corrosion and Material Protection, 1946, vol. 3, May, pp. 31-37). Continuation of a series of articles (see p. 39 A). The protection of steel from stress-corrosion by shot-peening, nitriding, cathodic treatment, and wet-hydrogen treatment are discussed.

ANALYSIS

(Continued from pp. 13 A-15 A)

Determination of Manganese and Chromium in High Chromium Steels. H. W. Tomb. (Iron Age, 1946, vol. 157, June 13, p. 64). A modification of F. Wilson Smith's perchloric-acid method of determining manganese in high-chromium steels and a method for determining the chromium are described.

Determination of Cobalt in High-Cobalt Products. R. S. Young and A. J. Hall. (Industrial and Engineering Chemistry, Analytical Edition, 1946, vol. 18, Apr., pp. 262-264). An analytical procedure is described for determining cobalt in which this element is separated from iron in high-cobalt products by one precipitation with tribasic sodium phosphate.

Carbon in Pig Iron. W. H. White. (Foundry, 1946, vol. 74, June, p. 109). A graph is presented showing the relationship between the silicon and graphitic carbon contents of pig-iron. There is a straight-line relationship up to about 13.75% of silicon.

Spectroscopic Determination of Carbon in Iron and Steel. O. V. Blank and N. S. Sventitsky. (Comptes Rendus (Doklady) de l'Académie des Sciences de

l'URSS, 1945, vol. 48, No. 4, pp. 252-255). Two variants of a method of determining carbon in iron and steel are described, one using the line C II 4267 and the other using line C III 2296-89.

Spectrographic Technique on the Charging Floor. J. T. Rozsa. (Iron Age, 1946, vol. 157, Mar. 28, pp. 42-46). The installation and lay-out of a spectrographic laboratory on the furnace charging floor at an integrated alloy-steel plant are described. Spectrographic determinations of carbon in open-hearth alloy-steel heats, and ladle analyses for manganese, silicon, chromium, nickel, molybdenum, copper, and tin, are conducted; in the electric alloy-steel furnaces these determinations are made after the melt-down and during the refining and final alloying stages. Analysis for seven elements can be carried out in less than 15 min., and for one element in 8 min. Details of the construction of the laboratory, the advantages of its location, the assignments handled, the technique and standards used, and operational and performance data are given.

Notes on the Quantitative Spectrum Analysis of Steels (Mo, Cr, Ti). P. Habitz. (Spectrochimica Acta, 1942, vol. 2, No. 3, pp. 158-169). The conditions governing the selection of the best line pairs in quantitative spectrum analysis are discussed. It is shown that there must be a minimum distance between adjacent lines. The conditions enumerated are applied to the selection of the best line pairs for the determination of molybdenum, chromium, and titanium in steels. The Cr 3128/Fe 3167 lines are recommended for determining up to 30% of chromium.

Some Observations on the Spectrum Analysis of Iron and Steel. A. Bardócz. (Spectrochimica Acta, 1944, vol. 2, No. 7, pp. 350-360). The results of research work in Buda-Pest from 1935 to 1937 on the spectrographic determination of silicon, manganese, chromium, and nickel in steel are reported. An apparatus for excitation in a gas atmosphere is described.

The Spectrographic Determination of Beryllium in Ordinary and Special Steels. O. Masi. (Spectrochimica Acta, 1940, vol. 1, No. 6, pp. 501-512). A procedure for the spectrum analysis of synthetically prepared solutions containing iron or steel and beryllium is described. Of twenty-five line pairs the following four are the best to use: Fe 2522.86/Be 2494.6; Fe 3440.61/Be 3321.1; Fe 3286.75/Be 3321.1; and Fe 2664.67/Be 2650.6. These pairs can also be used for the 15/10 and 25/20 chromium-nickel steels.

Spectrographic Determination of Boron in Steel. (National Bureau of Standards, Technical News Bulletin, 1946, Apr., No. 348, pp. 27-28). Brief particulars are given of three spectrographic methods for determining boron in steel; two are suitable for high-speed routine analysis, and the third is of the highest sensitivity for amounts down to 0.0001%.

The Spectrographic Determination of Boron in Steel. O. Masi. (Spectrochimica Acta, 1940, vol. 1, No. 5, pp. 462-470). The spectrum analysis of boron in steels by the solution method is discussed and a procedure is described which is accurate for contents exceeding 0.2%.

Spectrum Analysis of Metals by the Powder Method and the Determination of Small Concentrations of Boron in Steels. O. B. Falkova. (Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS, 1945, vol. 48, No. 3, pp. 179-181). A method for the spectrum analysis of metals in which the sample consists of fine filings is described. In the case of determining boron, a 200-mg. sample is placed in a shallow hole in an aluminium block and an A.C. arc is struck between the sample as one electrode and an Armo iron rod as the other.

The Determination of Niobium and Tantalum in High-Alloy Iron and Steel Specimens by Spectrum Analysis. O. Schliessmann. (Spectrochimica Acta, 1939, vol. 1, No. 3, pp. 239-248). A procedure for determining niobium and tantalum in high-alloy chromium-nickel steels is described. It is applicable for niobium contents exceeding 0.1%, and tantalum exceeding 1%. A single determination takes 2-3 hr.

The Quantitative Spectrum Analysis of Steels with Counter-Electrodes. T. Török. (Spectrochimica Acta, 1941, vol. 2, No. 1, pp. 26-31). The spectrum

analysis of steel using the sample as one electrode and another metal as the opposing electrode is discussed. An aluminium counter-electrode 3.5 mm. in dia. is recommended for a 1-mm. spark gap.

The Mass Spectrometer as an Analytical Tool. A. K. Brewer. (Mining and Metallurgy, 1946, vol. 27, Apr., pp. 207-209). The principle of the mass spectrometer is explained. Two mass spectrometers at the laboratories of the National Bureau of Standards and some work which has been done with them are briefly described. The apparatus is used to make accurate determinations of the composition of complex mixtures of hydrocarbons. Mixtures containing over thirty different compounds have been analysed.

An Automatic Time Switching Apparatus for Exposures in Spectrum Analysis. G. Balz and G. Reiniger. (Spectrochimica Acta, 1940, vol. 1, No. 4, pp. 323-331). The advantages of fully automatic control of the spark and the exposure in routine spectrum analyses are pointed out and a description is given of a switching apparatus which satisfies the requirements.

A Simple Apparatus for the Fully Automatic Control of All Switching in Spectrum Analysis. H. Brackebusch. (Spectrochimica Acta, 1941, vol. 2, No. 1, pp. 18-22). A fully automatic switching apparatus for controlling the pre-sparking and exposure times in routine spectrum analyses is described. This apparatus is not so elaborate and is less expensive than the one described by Balz and Reiniger (*see preceding abstract*).

A Time Switching Apparatus for the Automatic Control of Exposures in Spectrum Analysis. F. Wolbank. (Spectrochimica Acta, 1942, vol. 2, No. 3, pp. 150-157). An automatic switching apparatus for controlling the pre-sparking and exposure periods in spectrum analyses is described.

Time Switching Apparatus. P. H. Keck. (Spectrochimica Acta, 1944, vol. 2, No. 8, pp. 389-395). A description is given of a fully-automatic switching apparatus for controlling the pre-sparking and exposure times when using the spectrograph. It is constructed of commercially obtainable components.

Different Methods of Evaluating Spectra in Quantitative Spectrochemical Analyses. H. Kaiser. (Spectrochimica Acta, 1941, vol. 2, No. 1, pp. 1-17). A review of the various methods of evaluating spectra in spectrographic analyses is presented.

A Flame Method of Spectrochemical Analysis. W. A. Roach. (Journal of the Society of Chemical Industry, 1946, vol. 65, Feb., pp. 33-39). A flame method of spectrochemical analysis suitable for routine use is described and illustrated by detailed drawings. The material (*e.g.*, 25 mg. of leaf powder) is folded between filter paper, heated in ammonium-chloride vapour, and finally fed into an oxy-acetylene blow-pipe flame in front of a spectrograph. The method is suitable both for comparative diagnostic work and for quantitative analysis.

The Photometric Determination of Silicon in Steels. C. H. R. Gentry and L. G. Sherrington. (Journal of the Society of Chemical Industry, 1946, vol. 65, Mar., pp. 90-92). A method for determining silicon in steels using the silico-molybdate complex is described.

By the use of a number of alternative acid solvent mixtures, the range of steels which can be analysed by existing procedures is extended. The method is applicable to tungsten-bearing steels and to weld-metal deposits.

Color Determination of Tungsten, Titanium, and Columbium. C. M. Johnson. (Iron Age, 1946, vol. 157, Apr. 4, pp. 66-69). Colour determination of tungsten, titanium, and columbium in alloy steels, using the hydroquinone method, is discussed, and a rapid method is described for the quantitative determination of titanium in the presence of tungsten, columbium, and vanadium. Various analytical procedures and examples of mathematical computation are given.

Determination of Tungsten and Columbium in Stainless Steels. C. M. Johnson. (Iron Age, 1946, vol. 157, Apr. 11, pp. 66-68). To supplement the information given in a previous article upon colour determination by the hydroquinone method (*see* previous abstract) the author discusses the determination of tungsten and columbium together in stainless steels containing titanium, molybdenum, and about 18% of chromium and 10% of nickel.

A Simple Photo-Electric Absorptiometer. H. R. Clayton and B. A. Scott. (Journal of the Society of Chemical Industry, 1946, vol. 65, Apr., pp. 97-101). The construction and operation of a photo-electric absorptiometer of original design are described. The instrument can be readily constructed in the laboratory workshop from standard parts and is suitable for most routine colorimetric determinations at present carried out with more complicated and expensive apparatus.

Oxygen and Hydrogen in Steel Weld Metal. T. E. Rooney. (Welding, 1946, vol. 14, Apr., pp. 178-184; May, pp. 226-231, 236). Methods for determining oxygen and hydrogen in steel weld metal are described and those most suitable for industrial laboratories are indicated. The influence of the electrode coating on the amounts of these gases in the weld is also considered.

Rust Determination in the Presence of Steel. F. Gibadlo. (Iron Age, 1946, vol. 157, Apr. 18, pp. 58-59). A method has been devised by which rust can be preferentially dissolved in the presence of steel. The solvent is composed of potassium tartrate and potassium hydroxide. A procedure for determining rust by means of this solvent is described.

The Determination of Lime in Refractory Dead-Burned Magnesia. F. C. Gilbert and W. C. Gilpin. (Analyst, 1946, vol. 71, May, pp. 235-236). A procedure is described for the precipitation of calcium oxalate without removal of iron and aluminium in the analysis of dead-burned sea-water magnesia.

Most Economic Sampling for Chemical Analysis. C. W. Churchman. (Industrial and Engineering Chemistry, Analytical Edition, 1946, vol. 18, Apr., pp. 267-268). A statistical method of dealing with analytical data is described. It is known as "sequential analysis". It is intended to supply the answer to the problem: the chemist, by qualitative and elementary analysis and molecular weight determinations, has decided that a compound is one of two or more possibilities; how many determinations shall he make in order to obtain a certain degree of confidence in his analysis?

BOOK NOTICES

(Continued from pp. 40 A-41 A)

ALTIERI, V. J. "*Gas Analysis and Testing of Gaseous Materials.*" 8vo, pp. xi + 567. Illustrated. New York, N.Y., 1945: American Gas Association, Inc. (Price 45s.)

This book contains the following chapters: The Composition of Gases; Measurement of Quantity and Flow of Gas; Selection of Method of Sampling; Apparatus and Reagents; Common Operations; Calculations of Gas Analysis; Official Inspection and Testing; The Hempel Type of Apparatus and Method; The Orsat Apparatus and Its Modifications; The Elliott and Morehead Methods; The Shepherd Apparatus and Methods; Methods for Small Amounts of Nitric Oxide, Carbon Monoxide, Olefins, Oxygen, Hydrogen Sulphide, Cyanogen and Hydrocyanic Acid; Dusts, Sprays, Fumes, Mists, and Similar Dispersoids; Liquefaction and Distillation Methods of Analysis; The Determination of Sulphur Compounds; Light Oils in Gas; Naphthalene in Gas; Density and Specific Gravity; Analysis of Raw Gases.

EVANS, U. R. "*Metallic Corrosion, Passivity, and Protection.*" Second Edition. With an Appendix by A. B. Winterbottom. 8vo, pp. xxxiv + 863. Illustrated. London, 1946: Edward Arnold and Co. (Price 50s.)

The appearance of the Second Edition of Dr. Ulick R. Evans' "*Metallic Corrosion, Passivity, and Protection*"

will be generally welcomed as filling an important gap in scientific literature, for the First Edition, which appeared in 1937 and was reprinted in 1938, has been out of print for several years. Knowledge in this field has increased considerably during the intervening period. It is not surprising, therefore, that Dr. Evans has found it necessary to rewrite the major part of the book and that despite all his efforts at compression the text has increased in length by 15%. One important addition is an Appendix by Mr. A. B. Winterbottom, at one time a member of the Cambridge school of corrosion research, on optical methods for the determination of thin films on metals.

The arrangement of the subject-matter has been improved and extended as necessary to incorporate additional information, but it remains substantially the same. As before, each chapter is divided into three sections, dealing respectively with the scientific, technical and mathematical aspects of the branch of the subject under consideration. Thus, whether as a text-book for the student, a volume of reference for the research worker, or a source of information for the technician grappling with practical problems, Dr. Evans' work remains unsurpassed, for he brings to the subject a wealth of research experience and a fund of scientific knowledge which are peculiarly his own. One of his most pleasing characteristics, which immediately strikes the reader, is his sense of fairness when dealing with the work and views of other investigators whose opinions may differ, usually for a temporary period only, from his own. In this connection it is gratifying to note from Dr. Evans'

introduction that such substantial agreement has now been reached between the views of Dr. W. H. J. Vernon and his colleagues at the Chemical Research Laboratory, on the one hand, and those of the Cambridge University Corrosion Research Section, on the other, that the former group of investigators no longer considered it necessary to accept an invitation to contribute an appendix setting out their alternative views, as was done in the case of the First Edition.

It may be of interest to give a short list of the chapter headings, both because these indicate the scope of the book and because, as a basis of classification, it would be difficult to improve on them. They are as follows: I. Simple Examples of Corrosion and Passivity; II. Study of Thin Films; III. Oxidation at High Temperatures; VI. Corrosion in Moist or Polluted Atmospheres; V. Corrosion Not Involving the Absorption of Oxygen; VI. Corrosion of Ferrous Materials Involving the Absorption of Oxygen; VII. Corrosion of Non-Ferrous Materials Involving the Absorption of Oxygen; VIII. Influence of Stress, Strain and Structure; IX. Influence of Contacts and Crevices; X. Protection by Inhibitive Treatment of Water; XI. Protection by Chemical and Electrochemical Treatment; XII. Protection by Paints and Enamels; XIII. Protection by Metallic Coatings; XIV. Testing.

It is obvious that in a work of this magnitude covering such a wide field there may be certain minor points of detail which in the opinion of others might have been presented with some slight difference of emphasis or interpreted in a somewhat different manner. It would be churlish and unmannerly to approach the study of this book in such a captious attitude. Let us rather acclaim Dr. Evans' book as the masterpiece that it is and rejoice in the thought that, wherever the English language is spoken or understood, it will bear eloquent witness to the eminence of British scientific thought and research in the corrosion field. It is fitting to add that Dr. Evans has been ably seconded by his publishers and their printers who, despite the difficulties of wartime restrictions and the increase in the length of the text, have succeeded in producing an attractive book, which is much more wieldy than the old edition which it replaces.

J. C. HUDSON.

HENDRY, J. W. "*A Manual of Time and Motion Study.*" With a Foreword by B. S. Rowntree. 8vo, pp. viii + 215. Illustrated. London, 1946: Sir Isaac Pitman and Sons, Ltd. (Price 12s. 6d.)

The output of published literature on scientific management, of which time and motion study is an important part, has been of considerable magnitude during the past few years and there can be few people concerned with productive efficiency who are not aware of its importance, both during the man-power scarcity of the war period and the present term of change-over to peace production and the drive for exports.

However, in spite of, or perhaps because of, this copious supply of information on the subject only a small percentage of publications deal adequately with the basic principles of time and motion study which is the key to all productive efficiency.

Mr. Hendry's book, while covering the whole range of established time-study technique, lays great stress on the rating factor—this is most important since it is the "yardstick" of all assessments of physical effort; whether the method used by him, however, is the ideal one, is a debatable point, but it is one that is widely adopted in practice. It uses the principle of measuring the speed and effectiveness of the movements of the operator by equating them to a known standard of the expenditure of energy, e.g., a man walking a set distance and carrying a standard load in a given time. A fuller explanation of how this is transferred to, say, hand and arm, and general body movements in a more or less stationary position would have been of value to the reader and particularly to the student.

Although the greater proportion of this treatise deals with time study as distinct from motion study, the author 1946—ii

has not overlooked the fact that the two are complementary, and in spite of the fact that motion study is introduced and dealt with fully in the middle and later chapters, due references are made, when dealing with time study, to the importance of finding "the one best way" of doing the job, and this of course involves a searching analysis of layout and method, whether manual, mechanical, or a combination of the two. One of the most satisfactory features of Mr. Hendry's treatment of his subject is the underlying practical approach to problems of production management; armed with a system of proved principles for increasing efficiency he shows the reader how they can be applied to produce results in the practical field.

This application covers an average cross-section of mass production in engineering industry, machining, presswork, moulding, and assembly. The method of carrying out a time study is explained in detail and numerous examples are given concerning all phases of direct production and even auxiliary services such as trucking and inspection. The latter is often overlooked on the grounds that to speed-up would be dangerous since it would cause work-skipping—there may be some truth in this, but the converse, to speed-up because of an incentive, often means greater concentration. The question of applying incentives based on time study for such services as typing and canteen work is discussed and a case is made out for their inclusion under certain circumstances. Quite a large proportion of this treatise covers the staff work connected with time and motion study and suggestions for keeping records for cost control, producing charts for planning (machine loading), and building a library of synthetic rates, are given with examples.

The chapters on incentives and the psychological side of the subject are well worth close study since any system, however good, is doomed to failure if the people applying it have not got the right approach to the work-people and are unable to obtain their confidence and co-operation.

There is a chapter on the training of time-study personnel and a complete time-table covering a period of training for promising entrants into this branch of management. The sections dealing with motion study both with and without the camera, is comprehensive and very instructive. Under this heading there is a glossary covering a great number of operations and services in a representative engineering factory engaged on mass production. The author has set out typical examples of inefficiencies and has shown how they can be eliminated by change of method, appliance, or service, the changes being brought about by a careful study of the principles of motion economy applied with the all-important target of "waste elimination".

In conclusion it should be mentioned that this book of 200-odd pages deals most effectively and comprehensively with time and motion study economy in practice.

G. L. POTTER.

JACOBS, M. B. "*The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents.*" Second Revised Printing. 8vo, pp. xviii + 661. Illustrated. New York, N.Y., 1944: Interscience Publishers, Inc. (Price 42s.)

This book contains the following chapters: Industrial Hygiene and Industrial Poisons; Sampling; Measurement of Gas Volume and Quantity; Absorbers and Absorbents; The Chemical and Microscopic Estimation of Dust; The Chemical and Microscopic Estimation of Silica; The Dangerous Metals—Lead, Mercury and Arsenic; Other Harmful Metals; The Common Poisonous Compounds of Sulphur, Phosphorus and Nitrogen; Oxygen and Ozone; The Common Poisonous Compounds of the Halogens; Carbon Monoxide, Carbon Dioxide, Hydrocyanic Acid, and Cyanogen; General Methods for the Determination of Combustible and Solvent Vapours; Paraffin and Unsaturated Aliphatic Hydrocarbons; Benzene and the Aromatic Hydrocarbons; Halogenated

Hydrocarbons; Alcohols, Glycols, and Alcohol-Ethers, and Ethers; Acids, Esters, Aldehydes, and Ketones; Phenolic Compounds, Aniline and Derivatives; Chemical Warfare Agents.

LETORT, Y. "*Produits Refractaires. Matières premières. Fabrication. Usage.*" Préface de L. Guillet. 8vo, pp. viii + 199. Paris, 1945: Librairie Dunod. (Price 12s. 6d.)

This book deals with the raw materials for the production of refractories, their physicochemical transformations and the effect of high temperatures, the manufacture of refractory products, their properties and behaviour in service methods of testing, and the utilization of refractory products in ferrous and non-ferrous metallurgy.

LINCOLN, E. S. "*Electric Motors and Generators and Related Drives.*" 8vo, pp. ix + 381. Illustrated. New York, N.Y., 1945: Essential Books. (Price 18s.)

This book covers direct- and alternating-current motors of all kinds. The book gives data (much of it in tabular form) on the standard types of motor and generator, together with instructions for their installation and operation.

SIMON, W. H. "*American Arc Welding Patents.*" With a Foreword by W. F. Hess. Vol. I. "*Materials, Accessories, Electrodes, Welding Rods, Alloys, Electrode Holders, Welding Shields.*" Illustrated by A. Burras. 4to, pp. viii + 574. London, 1945: Bailey Bros. and Swinfen, Ltd. (Price £10 10s.)

Since the first world war, welding has been applied to an ever-increasing variety of metals and alloys extending

over numerous branches of engineering. It is not surprising, therefore, that welding development has occurred at a phenomenal rate, and that this is reflected in the number of patents issued and the confusion which exists regarding their classification in different fields. A need has existed for some time for a book which enables research workers and engineers to refer easily to the patent literature in the field of welding. In the compilation of this book the author has accomplished a somewhat difficult task in presenting the first volume of classified American arc-welding patents, although many patents on gas-welding rods and soldering fluxes are included. It lists the few basic patents when arc welding was in its infancy; classified patents up to April 1st, 1945, with an additional list of patents existing on July 1st, 1945. It covers a period of 63 years and contains 1,250 patents.

The book contains three sections:

1. Subject-matter index, which covers electrodes, welding rods and alloys, welding fluxes, chemical and metallurgical details, electrode holders, welding shields, and miscellaneous accessories. (72 pages).
2. Alphabetical list of inventors and assignees, with patent numbers and subjects. (66 pages).
3. Abstracts of patents in numerical order, with diagrammatic illustrations, filing date, duration and names of inventors and assignees. (424 pages). The abstracts give the claims which appear most significant, and the wording has been essentially maintained because of their legal significance.

Although the book deals with American patents, most worth-while British inventions are covered by patents in America. To a large extent, therefore, the book serves British requirements, has a definite historical value, and should find an important place in engineering and scientific libraries throughout the country.

E. C. ROLLASON.

REFRACTORY MATERIALS

(Continued from p. 18 A)

Mullite-Chrome Mixtures. W. F. Ford and W. J. Rees. (Transactions of the British Ceramic Society, 1946, vol. 45, Mar., pp. 125-136). Using mainly X-ray technique, a study has been carried out on fired mixtures of mullite with chromic oxide, chrome ore, and ferric oxide. Dissociation of mullite into its components has been shown to occur, the proportions by weight of these additions needed to produce complete dissociation decreasing in the above order. The improvement in resistance to ferruginous slags obtained on adding chromic oxide to sillimanite has been satisfactorily explained by the fact that ferric oxide forms a ternary solid solution with the chromic oxide and alumina. The higher ferric-oxide content of such ternary solutions explains the inferiority of chrome ore with respect to improving slag resistance.

Spalling of Silica Bricks. T. W. Howie. (Transactions of the British Ceramic Society, 1946, vol. 45, Feb., pp. 45-61). The amount of spalling occurring on heating silica bricks depends on the rate of heating and the temperature gradient developed. A heating rate greater than 5-6° C./min. is likely to produce spalling in normal silica bricks. Soft-fired bricks have a higher spalling-resistance than hard-fired bricks. For bricks with sp. gr. 2.37-2.38 the maximum safe rate of heating is about 8° C./min. The spalling resistance of silica bricks is closely related to their abnormal expansion at below red heat.

An Investigation into the Properties of Silica Brick. G. R. Rigby, R. P. White, H. Booth, and A. T. Green. (Transactions of the British Ceramic Society, 1946, vol. 45, Feb., pp. 69-105). The laboratory properties of nineteen silica bricks and two siliceous bricks were studied. The resistance to spalling when cooled from 200° and 400° C. was shown to be related to the

thermal expansion and elastic properties of the bricks. A method of determining the proportions of glass, quartz, tridymite, and cristobalite in silica bricks is described. There was a close relation between the quartz content and both specific gravity and percentage reversible expansion between 550° and 650° C. The results are given of the performance of certain brands of silica brick when used in open-hearth furnace roofs.

Carbon Products in the Steel Plant. F. Vosburgh. (Iron and Steel Engineer, 1946, vol. 23, May, pp. 60-67). Progress in the use of carbon bricks and blocks in blast-furnaces, pickling tanks, Cottrell precipitators, and in the chemical industry is reviewed.

Steel Foundry Refractories. J. L. Harrison. (Metal Treatment, 1946, vol. 13, Summer Issue, pp. 95-98). A commentary is presented on a recent paper by A. H. B. Cross on steel foundry refractories (see Journ. I. and S.I., 1945, No. II., p. 176A). Experience obtained with basic-lined ladles, lime-bonded and iron-oxide-bonded silica bricks in converters, and with sand additions to converters lined with (a) lime-bonded silica blocks, (b) iron-oxide-bonded silica bricks and (c) a rammed monolithic lining, are reported and discussed.

The Properties and Uses of Pyrometric Cones. (Refractories Journal, 1945, vol. 21, Nov., pp. 422-426; 1946, vol. 22, Jan., pp. 8-12; Feb., pp. 44-48). The history of the development of Seger cones is outlined and a description of the production of standard cones in America is given. It is stressed that cones measure "heat-work" or the effect of time and temperature combined. New standard machine-made cones to A.S.T.M. requirements are also described.

FUEL

(Continued from pp. 43 A-45 A)

The Ljungström Turbines in Germany. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 500: H.M. Stationery Office). A report is presented on a visit to the manufacturers of the Ljungström turbine in Germany; it contains a discussion of the causes of breakdowns of the blading system and of experience gained at a number of power-stations using these turbines.

Wartime Development in the Design of Boilers and Combustion Equipment in Germany. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 498: H.M. Stationery Office).

Boiler House at the Perry Furnace Plant of Interlake Iron Corporation. W. B. Clemmitt. (Blast Furnace and Steel Plant, 1946, vol. 34, May, pp. 602-607). A description is given of the new boiler plant at the blast-furnace and coke-ovens of the Interlake Iron Corporation at Erie. There are three boilers, each of the first two having capacities of 50,000 lb. of steam/

hr., and the third producing 75,000 lb./hr. They are of the three-drum water-tube type. Steam is produced at 175 lb./sq. in. at 450° F. Blast-furnace gas is the fuel for 80% of the steam; a further 10% is derived from coke breeze. There is also provision for burning coke-oven gas and bituminous coal.

Waste-heat Recovery. E. Watkinson. (British Engineering Export Journal, 1946, vol. 28, Apr., pp. 779-783; June, pp. 1049-1053). The principles of waste-heat recovery are explained, and the following types of economizers are described and illustrated: Green's vertical economizer, and ribbed-tube and needle-tube economizers. In the second part of the paper air heaters, waste-heat boilers, and recuperators are dealt with.

Waste-Heat Recovery. (Coke and Smokeless-Fuel Age, 1946, vol. 8, July, pp. 145-146). The type of diagram used by T. C. Finlayson and A. Taylor (see Journ. I and S.I., 1946, No. I., p. 58 A) is applied

to data on waste-heat recovery given by J. G. King and F. J. Dent (*see* p. 18 A) and the thermal efficiency of the regenerator is related to the heat-recovery efficiency of a whole coke-oven plant.

Waste-Heat Boilers in the Metallurgical Industries. J. A. Kilby and W. G. Cameron. (*Journal of the Institute of Fuel*, 1946, vol. 19, Aug., pp. 193-220). The application of waste-heat boilers to the metallurgical industries, with particular reference to the iron and steel industry, is defined and illustrated by detailed accounts of existing installations, the latter including almost every type of waste-heat boiler installation. Data on the Sulzer and Collin types of plant for dry-quenching coke are given, and the data obtained in the course of efficiency tests on waste-heat boilers working on open-hearth steel furnaces and a soaking furnace are presented in two appendices.

Material or Heat Transfer between a Granular Solid and Flowing Fluid. E. W. Thiele. (*Industrial and Engineering Chemistry*, 1946, vol. 38, June, pp. 646-650). This paper reviews work done on the computation of the transfer of material (or heat) when a fluid (liquid or gas) is passed through a granular bed, as occurs in the recovery of volatile solvents, in regenerators coupled with furnaces, and in gas masks.

An Electrical Geometrical Analogue for Complex Heat Flow. C. F. Kayan. (*Transactions of the American Society of Mechanical Engineers*, 1945, vol. 67, pp. 703-710). Through the medium of the resistance concept, the general similarity of "contour maps" for heat flow and electrical flow may be visualized. The electrical analogy permits ready study of simple and complex heat-flow conditions, which, because of distorted temperature conditions, would defy orthodox mathematical or graphical analysis.

Recuperative and Regenerative Furnaces. P. W. Dunn. (*Journal of the Junior Institution of Engineers*, 1946, vol. 56, July, pp. 257-269). Illustrated descriptions are given of refractory and metallic recuperators, open-hearth furnaces, mixers, and gas and air reversing valves.

Note on the Pneumatic Cleaning of Coals. G. Davin. (*Revue Universelle des Mines*, 1941, vol. 84, No. 2, pp. 79-84). The advantages of pneumatic as compared with hydraulic methods of cleaning coal are discussed, and an account is given of the principles of operation of the chief types of table. Attention is particularly directed to the Birtley table, employing sideways stratification, and its construction and operation are described at some length.

The Pneumatic Washing of Coals. C. Petit. (*Revue Universelle des Mines*, 1941, vol. 84, No. 9, p. 271). A brief description is given of the Type IV. Bruay-Soulary coal-cleaning plant, and reference is made to its advantages over earlier models from which the present design was evolved.

The De-Ashing of Coal by Combined Jig Washing, Froth-Flotation, and Extraction with Caustic Soda. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 522: H.M. Stationery Office). This report is an account of a process of preparing ultra-clean coal which was required for making

electrodes. The process was evolved by I.G. Farbenindustrie.

The Molecular Structure of Coal. I. Berkovitch and A. McCulloch. (*Fuel in Science and Practice*, 1946, vol. 25, Mar.-Apr., pp. 36-41; May-June, pp. 69-78). The effect on the carbonization products of heating coal with sulphur was investigated in three series of experiments. The most striking feature of the test data is the evidence provided that carbonization proceeds in a quite systematic and regular manner. The use of sulphur in the mass carbonized discloses the internal structure of the coal and its changes during carbonization, not in terms of the internal surface area, but in actual quantities of decomposition products.

Carl Alexander Mine, Baesweiler near Alsdorf—The De-Ashing of Coal by Froth Flotation and Acid Extraction and the Ruhrwerks Coal-Cleaning Process. (British Intelligence Objectives Sub-Committee, 1946: Final Report No. 523: H.M. Stationery Office).

Fuel Cost Economy at the Blast Furnace and Its Relation to Coal Selection and Preparation. W. M. Bertholf. (Blast Furnace and Coke Association of the Chicago District: Blast Furnace and Steel Plant, 1946, vol. 34, June, pp. 727-732, 740). Fundamental considerations of blast-furnace fuel costs are discussed with special reference to coal preparation, and tables, formulæ, graphs, and methods of calculation for the evaluation of coals are given.

Blast-Furnace Fuel Cost Economy. W. M. Bertholf. (Blast Furnace and Coke Association of the Chicago District: Steel, 1946, vol. 119, July 15, pp. 122-130). *See preceding abstract.*

Metallurgical Coke. Dr. Ing. A. Thau, *Didier Werke A.G., Berlin*. (British Intelligence Objective Sub-Committee, 1945, F.I.A.T., Final Report No. 408: H.M. Stationery Office). This report is concerned with recent developments and the present position in the use of low-rank coals, particularly those from Silesia, in the manufacture of metallurgical coke. The report consists primarily of three papers by Dr. A. Thau, translated from German into English by him. The titles of the papers are "Metallurgical Coke from Coal of Upper Silesia," "Metallurgical Coke from Non-Coking Coals with Special Reference to the Two-Step Carbonization Process," and "Experiences and Suggestions as to the Economy of Raw Materials for the Hydrogenation of Low-Temperature Carbonization of True Coal as well as for the Metallurgical Working-Up of Small-Grained Iron Ores."

Coking Industries in the Niagara Frontier. R. W. Pugh. (*Iron and Steel Engineer*, 1946, vol. 23, June, pp. 94-96). A description is given of the development and present capacity of the coke-oven plants on the Niagara frontier. These now comprise thirteen batteries with a total of 719 ovens which are controlled by three companies.

Modern Coke Ovens—The Basis of a Chemical Industry. E. V. O'Neill. (*Iron and Steel Engineer*, 1946, vol. 23, June, pp. 96-98). An account is given of the by-products produced in the coke-oven plants referred to in the preceding abstract.

Recent Developments in Producing By-Product Ammonium Sulphate. E. V. Schulte. (*Eastern*

States Blast Furnace and Coke Oven Association: Blast Furnace and Steel Plant, 1946, vol. 34, May, pp. 573-578, 625). A detailed description is given of a new saturator designed by the Koppers Company for use in the production of ammonium sulphate crystals of high quality. The saturator can deal with 48,000,000 cu. ft. of coke-oven gas per day. It greatly simplifies the control of operations and substantially reduces the operating costs.

Study of Metallurgical Coke Developments in Methods of Production and Testing—Röchling'sche Stahlwerke Völklingen, Saar. (British Intelligence Objectives Sub-Committee, 1945, F.I.A.T., Final Report No. 531: H.M. Stationery Office). A report is presented of a visit to the coke-oven plant of the Röchling'sche Stahlwerke with the object of obtaining information on any new developments connected with coke production. An attempt was made at this plant to increase the yield of benzol by modifying the gas take-off system. Holes were drilled in the top of each oven at 3 to 4 ft. intervals. Short pipes were introduced into these holes and connected to headers, and suction was applied to remove the gas. Each pipe was fitted with a liquid seal to prevent back pressure. Whilst the increase in benzol yield was problematical, the benzene yield was increased by 15-20%, and the total yield of light oil by as much as 25%. The report includes an unpublished paper by Dr. Henry Hoffman on the judging, testing, and evaluation of the physical properties of blast-furnace coke.

Mobile Coke-Briquetting Plant. (Iron and Coal Trades Review, 1946, vol. 153, July 19, pp. 107-108). A description is given of an electrically-driven self-contained briquetting plant mounted on a pneumatic-tired trailer. It is for briquetting coke dust wherever it accumulates—the mobility of the plant reducing the handling of the dust. It is designed to produce

1-3 tons/hr. of briquettes from previously ground coke screenings with pitch as a binder.

A New Coke Breaker. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 391: H.M. Stationery Office). A description is given of a coke-breaking machine at the Krupp Treibstoffwerk at Wanne-Eickel. This machine was designed for breaking slabs (about 50 × 40 cm.) of low-temperature-carbonization coke without a large yield of breeze.

Lurgi High-Pressure Gasification. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 521: H.M. Stationery Office). This report reviews the literature on the complete gasification of coal with steam and oxygen under pressure by the Lurgi process. It also describes the Lurgi plant visited, and makes a critical examination of the working results.

The Winkler Gasification Process. (Coal and Smokeless Fuel Age, 1946, vol. 8, July, pp. 155-158). The Winkler continuous gasification process, which uses a steam and oxygen mixture as the blast, is described and its performance in various German plants is discussed.

Gas-Fired Immersion Heating. R. M. Buck. (Midwest Industrial Gas Sales Council: Iron Age, 1946, vol. 158, July 11, pp. 46-52). Essential engineering data for calculating the size of the immersed coil of tubing and the heat-input requirements for the immersion heating of liquids in tanks are presented, and examples of the design calculations are given.

Fischer-Tropsch Plant of Hoesch Benzin, A.G. (British Intelligence Sub-Committee, 1945, F.I.A.T., Final Report No. 239: H.M. Stationery Office). A brief description is given of the plant and Fischer-Tropsch process at the works of Hoesch Benzin A.G., Dortmund.

PRODUCTION OF IRON

(Continued from pp. 45 A-46 A)

Humidity Measurement and Control in Steel and Allied Industries. O. J. Leone. (Iron and Steel Engineer, 1946, vol. 23, June, pp. 100-111). Illustrated descriptions are given of instruments for measuring humidity and their application to control the humidity of the air supplied to blast-furnaces and cupolas, to control the water vapour in atmospheres for heat-treatment, and to control rates of evaporation in enamelling, varnishing and baking process.

Thirty Years of Progress in the Metallurgy of Cast Iron. M. Derclaye. (Revue Universelle des Mines, 1942, vol. 85, No. 7, pp. 201-350). A comprehensive and well-illustrated survey is given of modern blast-furnace practice and of the changes made during the last thirty years. Progress has been made in improving furnace lines, in the use of preheated, dried, or oxygen-enriched air, and in providing better and more uniform coke. Large outputs have been made possible only by careful grading and proportioning of the charge.

Use of Scrap in the Blast Furnace. K. Neustaetter. (Blast Furnace and Coke Association of the Chicago District: Steel, 1946, vol. 119, July 1, pp. 122, 136-146). See p. 46 A.

Kembla's No. 2 Blast Furnace Blown-Out for Relining after Making 2,600,000 Tons of Iron. J. W. Thompson. (B.H.P. Review, 1946, vol. 12, Mar., pp. 1-3). An account is given of the blowing-out, using the nut-coke method, of No. 2 blast-furnace at the Kembla Works of the Australian Iron & Steel, Ltd., after a six-year campaign, during which over 2,600,000 tons of iron were produced. This furnace has a hearth 22 ft. in dia. Approximately 600 tons of salamander were run off through two holes designed to reach the centre-line of the furnace at depths of 5 and 7 ft., respectively, below the normal tap-hole level. Two sand beds of 960 tons' capacity were specially prepared for the reception of this material, the drainage of which occupied 2 hr. 47 min. Chemical analyses and other data are tabulated.

Dead Banking of Blast Furnaces. L. E. Riddle.

(Blast Furnace and Steel Plant, 1946, vol. 34, June, pp. 733-740). A method for the "dead" banking of blast-furnaces for an extended stoppage is described, in which combustion in the furnace is stopped by means of clean blast-furnace or natural gas introduced at the tuyeres through 2-in. pipes fed from an 8-in. circular manifold; on starting-up, the furnace is relit by oxygen lances. Many practical advantages are claimed, and extensive tables of costs are provided which show considerable savings over the older methods.

Recovery of Vanadium from Iron and Steel Plant Slags. (British Intelligence Objectives Sub-Committee, 1945, J.I.O.A., Final Report No. 23: H.M. Stationery Office). This is a report of an investigation to determine the amount and source of vanadium produced in Germany during the war. It described German practice in preparing vanadium-rich slags at steel plants and the method of recovering vanadic acid from these slags. Germany obtained about 2900

tons/annum of vanadium from iron and steel plant slags produced from iron ore containing about 0.10% of vanadium.

Experimental Electric Arc Furnace Smelting. H. S. Newhall. (Electrochemical Society: Metallurgia, 1946, vol. 34, June, pp. 91-93). Recommendations are made on the type of experimental electric furnace to use for research and pilot-plant operations on the smelting of ores and the manufacture of ferro-alloys.

Electric Smelting. N. F. Dufty. (British Steel-maker, 1946, vol. 12, July, pp. 342-345). The processes of making iron and the ferro-alloys in electric furnaces are briefly reviewed.

The Production of Aircraft Piston Rings by Powder Metallurgy. J. A. Judd. (Machinery, 1946, vol. 69, July 25, pp. 109-112). The press, the sintering process, and the sequence of operations in the manufacture of aero-engine pistons from electrolytic iron powder are described.

FOUNDRY PRACTICE

(Continued from pp. 46 A-48 A)

Control Tests for Grey Cast Iron. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 79, July 18, pp. 287-297; July 25, pp. 311-316; Aug. 1, pp. 337-345, 351). This Report consists of the recommendations of Sub-Committee T.S. 6 of the Technical Council of the Institute of British Foundrymen, which was appointed to "investigate and make recommendations on rapid forms of shop control tests mainly applicable to molten grey cast iron." Methods of moulding, quenching, and examining chill test-pieces, making shrinkage and fluidity tests, and of conducting analyses, mechanical tests, and temperature measurements are described.

Gamma Rays in the Service of Industry. F. Guyot. (Revue Universelle des Mines, 1941, vol. 84, No. 4, pp. 145-161). A comprehensive account is given of the technique for examining castings and forgings for internal defects by gamma rays derived from a radium source. A special radium holder, permitting free radiation in all directions, is described, and reference is made to the advantages of tin in place of lead as a material for intensifying screens. Details are given of the gamma radiography of some typical castings and assemblies, including the trunnions of a 20-ton basic-Bessemer converter.

Determination of "Gas Content" of Sand Cores. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 79, July 11, pp. 273-275). This short report is issued by Technical Sub-Committee 13 (Sands) of the Institute of British Foundrymen. It describes an apparatus and procedure for determining the volume of gas and the rate of evolution when samples of core sands are heated.

Experiences with Balanced Air Feed in the Cupola. T. H. Taft and H. A. Hallett. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 79, July 11, pp. 263-270; July 25, pp. 321-324). Experience gained in operating small cupolas with

balanced blast is reported. In order to provide a straight length of pipe to each of the four tuyeres to enable the air to be metered, the wind-box was built round the top of the cupola with a straight vertical connecting pipe leading down to each tuyere. This design is now known as the Pari-blast cupola. The lining wear was very uniform, but the metal was too hot until the iron/coke ratio of the charge was increased to 8. In order to operate the Pari-blast cupola successfully it is necessary to control other factors by weighing all the materials charged, measuring the coke-bed, and observing the descent of the stock level in the cupola. An automatic signalling device for indicating when there is room for another charge is described.

Investigations of the wear of the cupola lining were also made, and good results were obtained by using a mixture of good ramming ganister milled with 15% of crushed furnace coke and about 6% of water.

Notes on the Process of Gaseous Malleablising with Special Reference to the Use of Steam. D. M. Dovey. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 79, Aug. 1, pp. 347-351). A gaseous process for producing white malleable iron has been described by I. Jenkins and S. V. Williams, and by A. G. Robiette (see Journ. I. and S.I., 1945, No. II., pp. 80 A and 81 A). In this paper a process is described in which steam is admitted to the furnace, which results in a nitrogen-free atmosphere consisting mainly of carbon monoxide, carbon dioxide, hydrogen, and water vapour. The optimum conditions for operating this process were established by experiments on small charges, and these are discussed.

A Day in a Steelfoundry. V. C. Faulkner. (Foundry Trade Journal, 1946, vol. 79, July 25, pp. 317-318). A brief description of the organization at a modern steelfoundry is given with particular reference to the factors which promote *esprit de corps*.

The Production of "Grand Slam" Bomb Castings. B. Gray. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 79, Aug. 8, pp. 361-370). A comprehensive account is given of the methods adopted for casting very large steel bombs with

special reference to the moulding and core-making technique.

Core-Making Operations. J. H. List. (Iron and Steel, 1946, vol. 19, July, pp. 431-432). The making of a core for a pump impeller casting is described.

PRODUCTION OF STEEL

(Continued from pp. 48 A-50 A)

The Development of Alloy and Tool Steel Manufacture in India during World War II. P. H. Kutar. (Thirty-third Indian Science Congress: Blast Furnace and Steel Plant, 1946, vol. 34, June, pp. 741-745, 775-776). See p. 6 A.

Debatable Points in Steelworks Lay-Out. G. A. V. Russell. (Staffordshire Iron and Steel Institute: Iron and Coal Trades Review, 1946, vol. 153, July 26, pp. 141-144; Aug. 2, pp. 187-192). The layout of iron and steel works and its influence on the handling costs of raw materials and finished products are discussed. Six examples of layouts are described and the features of an ideal layout are pointed out.

Steel Slab Production. (Electrical Review, 1946, vol. 139, Aug. 2, pp. 167-171). Illustrated descriptions are given of several electrical appliances used in steel-making and slab rolling. These include lifting magnets, charging machines, ingot cranes and rolling-mill machinery.

Material Flow Diagrams for an Integrated Iron and Steel Works. H. W. Benschmidt. (Iron and Steel Institute, 1946, Translation Series, No. 282). This is an English translation of a paper which was published in Stahl und Eisen, 1943, vol. 63, July 29, pp. 529-537; Aug. 5, pp. 558-567. (See Journ. I. and S.I., 1945, No. II., p. 160 A).

Electric Furnace Design, Manufacture, and Application in Germany. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 533: H.M. Stationery Office).

Emergency Handling of Steel Plant Water Service. G. E. Stedman. (Steel, 1946, vol. 119, July 8, pp. 122-124). A brief description is given of the system of water-supply at the Fontana steelworks in California with special reference to the method of dealing with breakdowns.

FORGING, STAMPING, AND DRAWING

(Continued from p. 50 A)

The Manufacture of Armor Piercing Projectiles for the German Navy. (Combined Intelligence Objectives Sub-Committee, File No. XXVI-42, 1945: H.M. Stationery Office). This report covers the manufacture of armour-piercing projectiles from 28 to 40.6 cm. in dia. of low-alloy nickel-chromium-molybdenum-vanadium steel.

Report on Investigation of German Industrial Research and Development with Particular Regard to the Manufacture of Heavy Forgings and Large Bombs. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 476: H.M. Stationery Office).

German Steel Drum Industry. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 531: H.M. Stationery Office). The report is presented of the work of a team of experts which investigated German methods of manufacturing sheet steel kegs and drums.

Drop Forgings Industry. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 553: H.M. Stationery Office). Brief descriptions are given of the plant, the steels used, and the former production at 17 drop-forging works in Germany.

Survey of the Leading Manufacturers of Pressure Vessels. (British Intelligence Objectives Sub-Committee, 1945, F.I.A.T., Final Report No. 577: H.M. Stationery Office). The purpose of the survey here reported was to investigate and evaluate the most

important German manufacturers of pressure vessels so as to determine what innovations have been made in methods or manufacturing technique.

Manufacture of High Tensile Bolts. Bauer und Schaurte. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXXI-45: H.M. Stationery Office). A brief account is given of the methods of manufacturing high-tensile steel bolts and nuts at the works of Bauer und Schaurte, Neuss-Rhein, which is the largest bolt-manufacturing firm in Germany.

The Protection of Stainless Steel. (Chemical Age, 1946, vol. 55, Aug. 3, pp. 140-141). A brief account is given of methods of retaining the initial surface polish on stainless steel throughout subsequent processes, such as pressing and forming, as well as in transit. These methods include the use of wax paper, oiled paper, cellophane, and even ordinary newspaper between the die surface and the stainless-steel sheet.

Deep Drawing and "Bulging" Stainless Steel. J. E. Obernesser. (Steel, 1946, vol. 119, July 1, pp. 96-99, 114-116). An illustrated description is given of the sequence of processes in the drawing of stainless steel buckets and cans for dairy utensils.

Precision "Atmosphere" Forging. E. G. de Coriolis. (Steel, 1946, vol. 118, Apr. 8, pp. 90-94). A description is given of the sequence of processes in the manufacture of forged and welded hollow steel propeller blades. They are made of chromium-

nickel-molybdenum steel. Some of the blade components are heated four or five times, and are given only one blow in the press between each heat. All the heating is done in a protective atmosphere to prevent decarburization and oxidation.

Steel in Modern Building Construction. C. F. Block. (Steel, 1946, vol. 119, July 8, pp. 98-101, 127-130). Examples are given of the application of steel sections and pressings in the construction of houses, offices, and shops.

Forging Die Design. J. Mueller. (Steel Processing, 1946, vol. 32, May, pp. 306-308). The design of dies for forging single-throw crankshafts is discussed.

Mass Production of Deep-Drawn Parts. R. Dewert. (Revue Universelle des Mines, 1942, vol. 85, No. 5, pp. 154-164). Methods used in forming, heat-treating, and inspecting deep-drawn parts are outlined, and the field of application of the process is discussed.

The Mechanical Press for Deep-Drawing and Recent Improvements. P. Raskin. (Revue Universelle des Mines, 1942, vol. 85, No. 5, pp. 164-173). The most important features of a press are considered to be its accuracy, rigidity, speed and ease of operation, and safety. Some modern presses are described and illustrated.

Shaped Wire and Its Applications. V. H. Godfrey. (Steel, 1946, vol. 118, June 24, pp. 90-91, 117). Methods of drawing and rolling wire into various shapes and some of their applications are described.

Jones and Laughlin Winds over 4000 Miles of Wire per Day. (Steel, 1946, vol. 118, June 24, p. 106). A description is given of the wire-winding machines for the high-speed winding of wire 0.041 in. in dia. which have recently been installed at the works of the Jones and Laughlin Steel Corporation.

ROLLING-MILL PRACTICE

(Continued from pp. 50 A-51 A)

New Type of Continuous Billet Mill. T. Thomson. (Iron and Coal Trades Review, 1946, vol. 153, Aug. 9, pp. 225-229). To obviate the use of twist guides between stands in continuous billet mills, a fully continuous mill employing alternate horizontal and vertical stands has been designed and erected. It is for rolling billets $4\frac{1}{2}$ in. and $5\frac{1}{2}$ in. square and 3-in. slab billets. A description of the mill is given.

Rail Mills and Rail Mill Roll Design. R. E. Beynon. (Iron and Steel Engineer, 1946, vol. 23, June, pp. 53-80). A comprehensive review of the history of rail-rolling is presented. Descriptions of both old and modern mills are given together with details of auxiliary plant and equipment such as reheating furnaces, furnace-charging mechanism, tilting tables and mill guides.

German Wheel Manufacture. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 487: H.M. Stationery Office). An account is given of visits made to German works manufacturing all-steel wheels for agricultural machinery to discover the present state of the industry and whether any advanced methods are used.

New Hot Strip Mill. (Canadian Metals and Metallurgical Industries, 1946, vol. 9, May, pp. 20-22). A description is given of the new mill for rolling hot strip up to 56 in. wide which has recently been completed at the works of The Steel Company of Canada, Ltd. This mill, consisting of six 4-high stands, forms an extension to the 110-in. four-high plate mill which was completed in 1941. The equipment of the new mill includes slab-heating furnaces, a two-high scale breaker, rotary shear, run-out table, and piler.

Investigation of the Wear of Rolls during the Hot-Rolling of Wire and Strip. R. Tosterud and E. Stenfors. (Jernkontorets Annaler, 1946, vol. 130, No. 6, pp. 213-238). (In Swedish). An investigation of the wear of rolls in the rolling of wire and strip is reported. Its objects were: (a) to develop a method for the routine measurement and control of roll wear,

and (b) to relate the measured amounts of wear to other factors. Defects in the groove contour are due to normal wear, whilst surface defects are caused by the rolls being of unsuitable material. Full details are given of methods of accurately measuring the wear of both grooved and plain rolls. These methods make it possible to analyse the influence of different factors upon wear. A straight-line relationship is shown to exist between maximum radial wear and the quantity of material rolled, provided that the coefficient of friction is constant during the life of the roll. The surface of the roll grooves, which has a good polish when new, is roughened by the first few rods rolled, but after that it remains almost constant.

Two concepts, "relative wear" and "coefficient of wear," are introduced. The former is defined as the ratio of the maximum radial wear in μ to the corresponding length rolled in kilometres, and the latter as the ratio of maximum radial wear in μ to the amount of rolled material in tons. Formulae and curves are developed which can be used to plan a rolling mill for a given production as well as to estimate the time when the rolls will have to be renewed. The wear-resistance of different materials for rolls can also be quantitatively compared.

Experimental Research in the Cold Rolling of Metals. H. Ford. (Journal of the West of Scotland Iron and Steel Institute, 1944-45, vol. 52, Part IV., pp. 59-88). The experimental studies of cold-rolling made during the last few years are examined, the value of this work to the designer and operator is assessed, and the problems which urgently need investigation are specified. Excellent work has been done on questions troubling the mill operator, but no attempt has been made to collect this information or to render it suitable for general application. Further experimental work required can only be done on plant which is not on industrial production. The main fact which needs investigation is the ratio of the thickness of the material entering the rolls to the roll

diameter. The factor of strip tension urgently requires examination, for exact knowledge of the effect of back and front tension might lead to considerable modification in the design and operation of the present strip coiling gears.

Cold-Rolled Sheet Steel and Its Capacity for Deep-Drawing. P. Melon. (*Revue Universelle des Mines*, 1942, vol. 85, No. 5, pp. 108-114). A general account is given of the production of cold-rolled sheet steel, with special reference to the properties required in material intended for deep-drawing.

The Manufacture and Properties of Steel Sheets for Deep-Drawing. M. Gevers. (*Revue Universelle des Mines*, 1942, vol. 85, No. 5, pp. 115-121). An account is given of the methods used for producing cold-rolled steel sheet suitable for deep-drawing, and reference is made to factors which control grain-size and ageing phenomena in the product.

Deep Drawing Sheets. (*Iron and Steel*, 1946,

vol. 19, July, pp. 419-420). A brief description is given of the 80-in. four-high three-stand tandem mill for cold-reducing sheets up to 6 ft. wide at the works of John Lysaght, Ltd., Newport, Mon.

Tube-Making Plants—Mannesmann Röhrenwerke. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXXI-43 : H.M. Stationery Office). The steel-making and tube-making plants of the Mannesmann Röhrenwerke, Düsseldorf, are described.

Friction Sawing—Past and Present. J. M. Lewis. (*Iron and Steel Engineer*, 1946, vol. 23, June, pp. 81-90). The theory and practice of friction sawing are discussed with special reference to the severing of cold steel sections where the length of contact is appreciably more than that which can be successfully cut by blades other than circular friction saw blades. Data on blade design, cutting speeds and power requirements are presented.

HEAT-TREATMENT

(Continued from pp. 51 A-52 A)

Heat Treating and Processing Commercial Parts at J. W. Rex Company. (*Industrial Heating*, 1946, vol. 13, June, pp. 1036-1050, 1060). An illustrated description is given of the extensive heat-treatment plant of an American company undertaking a wide variety of work.

Practical Tool Room Heat Treatment. F. J. McMulkin. (*Iron Age*, 1946, vol. 157, June 6, pp. 60-65 ; June 13, pp. 56-59 ; June 20, pp. 64-68 ; June 27, pp. 55-59). A survey of heat-treatment techniques for tool steels is presented. In the first part tool steels are divided into twelve different classes and precautions to be taken during heating are pointed out. In the second part five methods of preventing the decarburization of tool steels during heat-treatment are described. The third part deals with quenching of tool steels and the precautions to be taken to prevent distortion and cracking, and the concluding part is concerned with salt baths and interrupted quenching.

Decarburization in Highly Stressed Steels. P. A. Haythorne. (*Iron Age*, 1946, vol. 158, July 4, pp. 52-61). The depth of decarburization which occurs in heat-treated low-alloy chromium-nickel-molybdenum steel used for highly stressed aircraft parts was investigated by hardness tests and by examining micrographs. Hardness measurements can be used to determine the extent of decarburization, provided the test area is properly selected and prepared.

Some Notes on Molten Baths. C. B. Rodgers. (*Machine Shop Magazine*, 1946, vol. 7, June, pp. 94-98). The use of molten lead and molten salt baths for heat-treating steel, and their advantages and limitations are discussed.

Calculation of Salt-Bath Electrodes. V. Paschkis. (*Industrial Heating*, 1946, vol. 13, May, pp. 784-794, 902). The calculations involved in the design of immersed-electrode salt-bath furnaces are explained.

New Carburizing Techniques Feature Operations at Canadian Acme Plant. (*Industrial Heating*, 1946, vol. 13, Feb., pp. 222-230 ; Mar., pp. 424-430, 460 ; Apr., pp. 610-616). The gas-carburizing and heat-treatment plant in the mass production of small parts for automobiles at the Toronto works of Canadian Acme Screw and Gear, Ltd., are described and illustrated.

Induction Heating for Production. (*Machine Shop Magazine*, 1946, vol. 7, July, pp. 96-103). The advantages and limitations of induction heating for the heat-treatment of steel parts are discussed and the factors limiting the flexibility of the process are pointed out.

Problems in High Frequency Induction Heating. E. H. Hulse. (*Iron Age*, 1946, vol. 158, July 18, pp. 60-64). The design of coils for the induction-heating of round bars and objects of irregular shape is discussed and formulæ for making the calculations are presented.

Induction Heating. J. M. Lee. (*Pacific Coast Electric Association : Iron and Steel*, 1946, vol. 19, July, pp. 437-440). A variety of induction-heating equipment for metallurgical purposes is described and illustrated.

Induction Hardening Ram-Taper Areas of Heppenstall Steam-Hammer Piston Rods. (*Industrial Heating*, 1946, vol. 13, Apr., pp. 628-632). A brief description is given of the induction-hardening process which is applied to the surface of piston rods in steam hammers. The heating unit, incorporating a water spray, surrounds the rod and passes upwards over the part which is to be hardened. A surface hardness of 495 Brinell, falling away to 302 Brinell at a depth of $\frac{1}{4}$ in., is obtained.

New Annealing Plant for Steel Strip in Coils at the Whitehead Iron and Steel Co., Ltd., Newport, Mon. B. Jones and I. Jenkins. (*Iron and Steel Institute*, 1946, this Journal, Section I). An electric anneal-

ing unit for the annealing of steel strip in coils in a controlled atmosphere is described. The plant was designed for an output of 1000 tons/week, and is worked in conjunction with a similar and older installation with an output of approximately 500 tons/week. The compact layout of the plant, which includes sixteen annealing furnaces, recuperator and cooling pits, and controlled atmosphere units, is referred to. Details of the annealing cycle are given, and the causes of staining of the steel charge by unsuitable annealing gas and rolling oils are discussed. There is a close control of temperature in both the furnace and the charge. Tests have been made on the properties of low-carbon-steel strip annealed in various parts of the annealing container, and an

Appendix is given on the effect of annealing temperature on the properties of heavily cold-reduced mild steel strip. It is shown that there is a range of annealing temperatures above 600° C. in which the work-hardening effects are effectively removed, good properties are obtained, and a suitable grain-size can be imparted to the steel.

Heat-Treatment in Deep-Drawing Operations. R. Boone. (*Revue Universelle des Mines*, 1942, vol. 85, No. 5, pp. 133-141). The requirements of furnaces for annealing steel sheet and stampings are outlined and an account is given of some French equipment for annealing in closed containers or in protective atmospheres.

WELDING AND CUTTING

(Continued from pp. 52 A-53 A)

The Principles of Welding Metallurgy. J. Candlish. (Australian Welding Institute: Australasian Engineer, 1946, May 7, pp. 36-46). This paper is in two parts; the first explains general metallurgical principles concerning the solidification of pure metals and alloys, and the construction of equilibrium diagrams. In the second, these principles are applied to explain what happens during the heating and cooling of welds.

Metallurgy for Welders. D. Llewellyn. (Welding, 1946, vol. 14, July, pp. 315-320, 328). In the first of a series of articles designed to help welders to increase their knowledge of the behaviour of metals during welding and subsequent cooling the author describes sulphur printing and macro-etching, and discusses practical examples of faults detected by these methods.

Welding of 3½% Ni-0.40% Carbon Class A_n Steel Forgings. B. Ronay. (Welding Journal, 1946, vol. 25, June, pp. 495-503). An investigation is described the purpose of which was to develop a welding procedure for repairing hollow forged steel marine propeller shafts with walls from 2 to 6 in. thick, the steel containing carbon 0.35-0.45%, manganese 0.6-0.9%, and nickel 2.75-3.75%. Details are given of a satisfactory method which left the properties of the joint fully comparable with those of the unaffected parent metal.

Recommended Practices for Automotive Flash-Butt Welding (Tentative). (American Welding Society, 1946, Pamphlet D8.1-46T). The Automotive Welding Committee of the American Welding Society has prepared these tentative standard specifications, which represent the consensus of opinion of the American automobile manufacturers on the best methods of making flash-butt welds.

Some Aspects of the Welding of Stainless Steels. J. A. McWilliam. (Sheet and Strip Metal Users' Technical Association: Sheet Metal Industries, 1946, vol. 23, July, pp. 1369-1374, 1382). Recommendations on welding procedures for stainless steels are made.

Welding Stabilized 18-8 Stainless. R. J. Hafsten. (Iron Age, 1946, vol. 158, July 11, pp. 60-64). The effect of titanium and columbium on the micro-

structure and corrosion resistance of welded stainless steels is discussed. The best results are obtained with columbium-bearing 18/8 stainless steel electrodes or welding rods on columbium-stabilized stainless steel sheet. The failure of gas-welded titanium-stabilized specimens in bend tests appears to be caused by ferrite or a ferrite-carbide structure in the grain boundaries.

Welding Multi-Layer Steel Pressure Vessels. (Materials and Methods, 1946, vol. 23, June, pp. 1578-1582). A series of illustrations with explanatory titles describe the preparation and welding operations in the manufacture of cylindrical steel pressure vessels consisting of several layers of thin steel plate, each layer being seam-welded and ground in turn.

Fundamentals Affecting the Bond in Pressure Welds. L. Fine, C. H. Maak, and A. R. Ozanich. (Welding Journal, 1946, vol. 25, June, pp. 517-529). Factors affecting the quality of oxy-acetylene pressure welds in tubes and bars are discussed and sections of welds are studied by etching with an alkaline chromate solution which reveals dissolved oxygen in the metal.

Observations on the Appearance Welding of Malleable Castings. H. A. Schwartz, I. Young, and J. Hedberg. (Proceedings of the American Society for Testing Materials, 1945, vol. 45, pp. 618-625). The microstructures obtained when surface defects in malleable iron castings are welded by various techniques are discussed.

Procedures for Arc Welding Gray Iron Castings. C. E. Phillips. (Welding Journal, 1946, vol. 25, June, pp. 547-548). Details are given of the technique adopted to fill a cavity in a large grey-iron casting by welding, the object being to avoid the formation of hard spots.

De Forest Brittle Temperature. P. R. Shepler. (Welding Journal, 1946, vol. 25, June, pp. 321-S-332-S). The temperature of the transition of a number of steels from ductile to brittle behaviour was studied by obtaining load-deflection curves in bend tests at successively decreasing temperatures on notched specimens. Welded and unwelded specimens of ship-plate were tested. Deposited weld metal had

a lower transition temperature, or greater ductility, than the parent metal in the case of unkilld steel. With hand-welded unkilld steel plates the parent metal 1 in. from the centre of the weld was the most brittle, the metal at the weld centre was the most ductile, and the parent metal 5 in. from the weld was in an intermediate category.

Boiler Tubing Fabricated by Oxy-Acetylene Pressure Welding. (Welding, 1946, vol. 14, July, pp. 313-314). A description is given of the equipment and process for making oxy-acetylene butt welds in boiler tubes. The process is similar to "Uniwelding" which has already been described (*see* Journ. I. and S.I., 1946, No. I., p. 77 A).

Some Results of Advances in Welding and Radiography on the Welding of Pressure Vessels. O. R. Carpenter. (Welding Journal, 1946, vol. 25, June, pp. 531-542; Industrial Radiography and Non-Destructive Testing, 1946, vol. 5, Summer Issue, pp. 9-17). Radiographic and supersonic methods of testing welds in pressure vessels are discussed and a detailed account is given of defects caused by the oxidation of sulphide inclusions in thick plates and the method by which these were studied. In particular, the results obtained with the Sperry Supersonic Reflectoscope are described in detail. It was found that the Reflectoscope could be used to examine the edges of thick plates before welding and determine whether more than a permissible amount of segregation existed.

Improvement of the Notch Impact Resistance of Gas-Welded Joints. A. Matting and H. Koch. (Welding Journal, 1946, vol. 25, June, pp. 359-S-360-S). In order to establish the best technique for obtaining high impact test results on oxy-acetylene-welded thick plate of German boiler quality, tests were made with different types of joint preparation with and without subsequent peening. The best results were obtained with a low-alloy steel welding rod, taking care not to overheat, and then peening the top of the weld. (This is an abridged translation of a

paper which appeared in Autogene Metallbearbeitung, 1942, vol. 35, Apr., p. 93).

Residual Stresses in Welded Structures. W. M. Wilson and Chao-Chien Hao. (Illinois University, 1946, Engineering Experiment Station Bulletin Series No. 361). The object of the investigation reported was to determine the magnitude of the thermal stresses caused by welding, and to determine the strength and ductility of the resulting weld. The specimens were limited to welded plates of A.S.T.M. Steel A7 (a 0.26%-carbon steel). The strength and analyses were determined by analyses and by tests. Some specimens were tested statically and others in fatigue.

A Method for the Measurement of Residual Welding Stresses. J. L. Meriam, E. P. DeGarmo, and F. Jonassen. (Welding Journal, 1946, vol. 25, June, pp. 340-S-343-S). A procedure is described by which strain gauges are used to determine the residual stresses in welded parts of ships under shipbuilding conditions.

Induction Heating Brazes Tool Tips. T. A. Vernor and E. F. Adams. (Industrial Heating, 1946, vol. 13, May, pp. 807, 822). The equipment used to apply induction heating to braze alloy steel tips to mild steel tool shanks is described.

Special Oven Developed for Drying Extruded Welding Electrodes. (Industrial Heating, 1946, vol. 13, May, pp. 839-843). Descriptions are given of a flux extrusion plant for coating welding electrodes and an oven with a continuous chain conveyor for drying them. In this oven the chain is arranged so that seven passes are housed in an insulated chamber 25 ft. long with a maximum height of 4 ft.

Flame-Cutting Stainless Steel. G. E. Bellew. (Iron Age, 1946, vol. 158, July 11, pp. 42-45). The equipment and process recently developed for flame-cutting stainless steel are described. A suitable flux in the form of a fine powder is fed into the oxygen of a standard oxy-acetylene cutting torch, and this enables clean cuts in stainless steel to be obtained.

CLEANING AND PICKLING OF METALS

(Continued from pp. 29 A-30 A)

Cleaning and Acid Pickling. (Wire Industry, 1946, vol. 13, July, p. 382). Particulars are given of the properties of a detergent known as "Teepol X" which is used in alkali and acid cleaning and pickling processes. It is the first example of a synthetic detergent of the alkyl-sulphate type to be manufactured on a large scale in Great Britain.

Sodium Hydride Descaling. E. L. Cady. (Materials and Methods, 1946, vol. 23, May, pp. 1278-1283). The sodium-hydride descaling process has already been described by L. W. Townsend (*see* Journ. I. and S.I., 1946, No. I., p. 48 A). In the present paper the plant for descaling stainless and other alloy steels at the works of the Carpenter Steel Company is described.

Now We Can Tell. A. M. Valz. (Du Pont Maga-

zine, 1946, vol. 40, Mar., pp. 12-13, 19). A brief description is given of the Du Pont sodium-hydride descaling process (*see* Journ. I. and S.I., 1946, No. I., p. 48 A).

Sodium-Hydride Descaling and Desanding of Ferrous Castings and Forgings. (Industrial Heating, 1946, vol. 13, May, pp. 796-802). The process of removing sand and scale from castings and forgings with a bath containing molten caustic soda and a small addition of sodium hydride is described.

Descaling and Desanding Gray Iron Castings. (Steel, 1946, vol. 119, July 15, pp. 104, 142). The descaling process involving a sodium hydroxide bath containing sodium hydride has been applied to removing sand from grey iron castings. The work is first immersed in the bath which is held at 700° F.

It is then quenched in water, dipped in dilute sulphuric acid for not longer than 1 min., and finally immersed

in a weak sodium cyanide bath at 200° F. to neutralise any remaining acid.

COATING OF METALS

(Continued from pp. 30 A-31 A)

German Electroplating Industry. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 429: H.M. Stationery Office). A team visit to electroplating plants in Germany and its report is presented. It examines the application of electro-deposition to war purposes and gives an outline of the German plating industry.

Chromium Plating Practice in the Facing of Press Dies. E. A. Ollard and E. B. Smith. (Sheet Metal Industries, 1946, vol. 23, June, pp. 1129-1141, 1159). A full account is given of the processes necessary for plating a thick adhesive layer of chromium on to steel dies.

Electroplated Pipe Interiors. S. G. Bart. (Steel, 1946, vol. 118, June 24, pp. 96-97, 148). A brief description is given of an electroplating process for applying nickel to the inside surface of steel tubes.

"Dry" Galvanizing. H. Bablik. (Metal Industry, 1946, vol. 68, June 21, pp. 487-489). In "dry" galvanizing the flux solution is spread over the surface of the part to be galvanized and is dried before the part enters the zinc bath. This process is described with special reference to the part played by aluminium in the bath.

Electroalgalvanizing. H. Roebuck and A. Brierley. (Electrodepositors' Technical Society: Metal Industry, 1946, vol. 69, July 19, pp. 50-53). A description is given of the Brylanizing process for coating steel wire with very pliable pure zinc. The process can best be considered as a unit for producing a zinc-sulphate electrolyte from roasted zinc-blende ore and using this electrolyte to deposit zinc (99.9%) directly on to travelling wire cathodes. It is possible to deposit heavy coatings on large base sizes of either mild or high-carbon steels to be hard-drawn to finished products.

Welsh Tinplate Industry. J. H. Mort. (Iron and Steel, 1946, vol. 19, July, pp. 413-418). The article on the Welsh tinplate industry (see p. 30 A) is concluded, Parts II. and III. dealing respectively with the present economic situation and remedial measures.

A Protective Chemical Treatment for Tinplate. R. Kerr. (Journal of the Society for Chemical Industry, 1946, vol. 65, Apr., pp. 101-107). A description is given of a protective treatment for tinplate which consists of immersing the tinplate for 20 sec. at 85° C. in an alkaline phosphate-chromate solution containing a penetrating agent; this gives it an invisible film coating which affords protection against blackening by sulphur-containing foods. With this coating the amount of tin absorbed by the food during storage is less than that in cans made from untreated tinplate.

Bi-Metal Tubing. (British Intelligence Objectives Sub-Committee, 1945, F.I.A.T. Final Report No. 595: H.M. Stationery Office). Descriptions are given of

the methods employed by two German works to produce steel tubes clad with copper or bronze either on the inside or the outside, or on both sides.

Rustproofing Process Proves Advantageous to Fabricators. G. P. Muir. (Steel Processing, 1946, vol. 32, May, pp. 298-300). The Banox process of applying a thin phosphate coating on steel is described. Its principal advantages are low cost, good adherence, and pliability. It can be applied to steel before forming and stamping and the coating will not crack during these operations.

Finish Durability Improved with Vitreous Phosphate Coating. C. T. Roland and H. I. Rosenbloom. (Steel, 1946, vol. 118, June 17, pp. 122-129). Particulars are given of the "Banox" coating which can be applied to zinc or steel by dipping the part into Banox solution at room temperature; this creates an amorphous phosphate film on the surface of the metal. The coating forms an excellent base on which to apply paint and by itself it offers a high resistance to oxidation for a short time.

A New Express Method of Phosphating Steel Parts. G. V. Akimov and A. A. Ulyanov. (Comptes Rendus (Doklady) de l'Académie des Sciences de l'U.R.S.S., 1945, vol. 49, No. 7, pp. 497-499).—A brief account is given of a method of improving phosphate coatings on steel by producing a more uniform, thin, and porous film, and subsequently impregnating it with a chromate solution and solutions of organic substances.

The Treatment of Steel Strip Prior to Fabrication. W. F. Coxon. (Sheet and Strip Metal Users' Technical Association: Sheet Metal Industries, 1946, vol. 23, July, pp. 1307-1310). A strong case is made out for the phosphatizing, lacquering or tinning of strip before pressing and stamping as well as for the development in Great Britain of plant for electrolytic polishing.

Phosphating Metallic Surfaces. I. History and Pre-Treatment. W. G. Cass. (Chemical Age, 1946, vol. 55, July 6, pp. 5-8; July 13, pp. 35-38; July 20, pp. 67-70; July 27, pp. 101-104). The history and patents relating to the application of phosphate coatings to prevent the corrosion of iron and steel are reviewed with notes on anti-trust and patent litigation in the United States.

Metallgesellschaft A.G., Frankfurt, Chemicals for Phosphating Iron and Steel. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 257: H.M. Stationery Office). A brief account is given of the method of preparing the liquors used by Metallgesellschaft A.G. for phosphatizing steel sheet.

Production of Steel-Backed Lead-Bronze Bearings. (Machine Shop Magazine, 1946, vol. 7, July, pp. 34-43). A detailed description is given of the sequence of

processes in the manufacture of lead-bronze bearings with a steel backing. To bond the alloy to the steel, the shell, containing the required weight of alloy in chip form, is mounted on a mandrel and spun inside a small furnace. When the alloy melts it is forced into a homogeneous mass and makes an intimate bond with the steel shell which surrounds it.

Manufacture of Vitreous Enamelled Sheet Iron Baths in Germany. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 344: H.M. Stationery Office). A brief account is given of the methods of pressing and enamelling sheet iron baths at the works of Herding and Mentrup, and of Franz Kaldewei, both at Ahlen in Westphalia.

German Glass or Enamelled Lined Equipment on Mild Steel and Cast Iron for Chemical, Food, Drink, and Allied Industries. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 569: H.M. Stationery Office). An account is given of the methods used by German firms for lining steel tanks, vessels, and pans with glass and enamel so that they can be used for transporting wine, beer, and milk.

Interim Descriptive Statement on the Leaching-Rate Test for Ships' Anti-Fouling Compositions. The Joint Technical Panel on the Leaching-Rate Test of the Marine Corrosion Sub-Committee. (Iron and Steel Institute, 1946, this Journal, Section I).

This preliminary statement on the leaching-rate test for anti-fouling paints has been prepared in response to a demand from a section of the paint trade and is the result of work by investigators attached to the Marine Corrosion Sub-Committee of The Iron and Steel Institute and the British Iron and Steel Research Association, and by their collaborators on the Admiralty Corrosion Committee.

The test is designed to assess the value of anti-fouling compositions by measuring the rate of loss of toxic ingredients from the paint surface during immersion in sea-water. Originally developed in the U.S.A. for application to anti-fouling compositions containing cuprous oxide as the only toxic ingredient, the test is being adapted for use on formulations containing more than one toxic constituent and in particular on those with copper and mercury, to which type most of the British proprietary compositions belong.

In conducting the test, small glass panels coated with the anti-fouling compositions under test are stored in sea-water and transferred periodically into the leaching apparatus, where they are subjected to agitation (by bubbling) in a definite amount of sea-water for a standard time; the toxic substances leached into the water are then determined. It is essential that the ratio:

$$\frac{\text{Paint area} \times \text{Test duration}}{\text{Volume of sea-water used for leaching}}$$

is kept constant. The determination by colorimetric methods (using a "Spekker" photo-electric absorptiometer) of the small amounts of copper and mercury leached into the sea-water is described.

In the simplest case of anti-fouling compositions containing cuprous oxide only, it is known that a steady loss of copper of about 10 microgrammes/sq. cm./day is effective in preventing fouling. This is termed the "critical leaching rate" for copper. The critical rates for mercury, for copper and mercury in the same composition, and for other anti-fouling poisons are not yet sufficiently defined for statement, although it is known that the rate for mercury is less than half of that for copper.

The statement emphasizes that, at present, exact standardization of the test has not been achieved, nor has its precise significance in relation to service behaviour been fully determined. Further work on points requiring elucidation is being carried out in several laboratories.

The Formulation of Anti-Corrosive Compositions for Ships' Bottoms and Underwater Service on Steel. Part II. F. Fancutt and J. C. Hudson. (Iron and Steel Institute, 1946, this Journal, Section I). A second series of raft tests by the Marine Corrosion Sub-Committee on anti-corrosive paints for underwater use on ships' bottoms has confirmed the earlier results and enlarged them considerably. One hundred and twenty-seven new formulated anti-corrosive paints were made for the purpose and comprised various combinations of mixtures of 8 different media with 13 different pigments. On the basis of the results, paint No. 173, pigmented with a mixture of 2 parts of basic lead sulphate and 1 part each of white lead, Burntisland red, and barytes, and bound in a modified phenol-formaldehyde/litho-oil medium is suggested for general use at this stage. Several other paints gave an even better performance in the raft tests than paint No. 173 and merit further investigation. Paints in a chlorinated rubber medium were outstanding but certain technical difficulties need to be overcome before these can be used effectively on a practical scale.

Action of Antifouling Paints, J. D. Ferry and D. E. Carritt. (Industrial and Engineering Chemistry, 1946, vol. 38, June, pp. 612-617). The solubility and rate of solution in sea water of cuprous oxide, the most commonly used poison in anti-fouling paints, was measured. The solubility is proportional to the hydrogen-ion concentration and agrees with the solubility calculated from data of a thermodynamic nature, assuming that the dissolved copper exists as the complex ions CuCl_2^- and CuCl_3^{--} . The rate of solution of cuprous oxide in sodium chloride-nitrate-borate buffer solutions is proportional to the hydrogen-ion concentration and is a linear function of the square of the chloride-ion concentration at constant ionic strength.

PROPERTIES AND TESTS

(Continued from pp. 54 A-60 A)

Torsional vs. Tensile Properties of Steels. M. C. Fetzer. (Steel, 1946, vol. 118, June 24, pp. 92-94, 118-123). The use of tensile and torsional tests to study the properties of steels was studied by comparing the results obtained when applying these tests to Armco iron, steels with carbon contents up to 0.95%, and 18/8 stainless steel. It was found that the tensile test is the better method for determining yield points, whilst the torsional test provides more fundamental information on the strength and ductility.

25-Ton Universal Hydraulic Testing Machine. (Engineering, 1946, vol. 162, July 26, p. 81). An illustrated description is given of a compact universal hydraulic testing machine with which tensile, compression, shear, and bend tests can be made.

The Importance of Ultimate Extension as an Engineering Property of Materials. A. Fisher. (Metallurgia, 1946, vol. 34, June, pp. 77-84). The shortcomings of the percentage elongation after fracture and the advantages of the ultimate extension before fracture as criteria for the strength and toughness of metals are discussed. The importance is stressed of using the ultimate extension in strength calculations for alloys having a duplex and interlocking type of structure the different constituents of which possess different elastic moduli and different stress-strain curves, especially when the part is to be in service under conditions of specific strain—a condition far more common in engineering structures than is generally supposed.

Using Electronics to Solve Stress-Strain Problems. (Machinist, 1946, vol. 90, July 6, pp. 507-509). A description is given of an electronic apparatus for determining the actual stresses required to pull a material to its elastic limit, for evaluating the modulus of elasticity, and for recording stresses induced in either static or moving elements without the use of slip rings or other physical connections.

The Versatility of the Chevenard Differential Dilatometer with Photographic Recording. V. Mathien. (Revue Universelle des Mines, 1942, vol. 85, No. 3, pp. 57-71). A comprehensive account is given of the construction and operation of the Chevenard differential dilatometer and of the interpretation of the curves obtained with the instrument. Modifications to the original instrument include the rotation of the head around a horizontal axis, the provision of windows allow the insertion of wedges, changes in the method of attaching the head to the body, and the mounting of the tubes in a vertical position.

Measurement of Torque Transmitted by Rotating Shafts. B. F. Langer. (Transactions of the American Society of Mechanical Engineers, 1945, vol. 67, pp. A-39-A-42). Various torque measuring devices are briefly described and a more detailed description is given of a recently developed magnetic coupled torque-meter. The latter machine is particularly applicable where high speeds and severe operating conditions are encountered.

New Form of Notched-Bar Test Piece. W. E. Woodward. (Engineering, 1946, vol. 162, Aug. 9, p. 123). The author describes the tests leading to the design of a new Izod specimen which requires less machining than the specimen given in British Standard No. 970. The former is 5.5 in. long and 0.45 in. in dia., and it has three 75° grooves cut in it 1.1 in. apart.

Practical Electric Resistance Strain Gage Procedures for Structural Tests on Ships. W. V. Bassett. (Proceedings of the American Society for Testing Materials, 1945, vol. 45, pp. 651-666). Procedures for using electrical strain gauges to study welding stresses in ships, which give results within ± 500 lb./sq. in., are described.

Electric Strain Gauges. A. B. White. (Electrical Review, 1946, vol. 139, Aug. 2, pp. 175-176). The principles of the electric strain gauge are explained and some modern gauges, including one for use at elevated temperatures, are described.

Industrial Electronic Measuring Equipment. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 564: H.M. Stationery Office). Information is given on the design of a number of German-made electronic instruments including an acoustic strain gauge.

Summary Report on the Joint E.E.I.-A.E.I.C. Investigation of Graphitization of Piping. S. L. Hoyt, R. D. Williams, and A. M. Hall. (American Society of Mechanical Engineers: Welding Journal, 1946, vol. 25, June, pp. 332-S-339-S). The results of numerous investigations on the graphitization of steam pipes operating at high temperature and pressure are summarized. Silicon-killed steels and steels killed with not more than 0.5 lb. of aluminium per ton are relatively immune from graphitization. A steel containing 0.50-1.00% of chromium and 0.50% of molybdenum is recommended, and, after welding, a stress-relieving treatment at above the A_{c1} temperature should be applied. Welded joints exhibiting some graphitization can generally be successfully treated by normalizing at 1650-1700° F.

Micro-Hardness Testing. E. B. Bergsman. (Metal Industry, 1946, vol. 69, Aug. 9, pp. 109-112). A micro-hardness testing device for use with an ordinary metallurgical microscope is described (*see* Journ. I. and S.I., 1944, No. II., p. 112 A) and examples of its application are given.

Development and Use of Permanent Magnet Materials. D. Hadfield. (Sheffield Metallurgical Association: Iron and Coal Trades Review, 1946, vol. 153, July 19, pp. 89-92). Recent discoveries of various alloys possessing special magnetic properties, and their manufacture, are discussed, in particular, those magnetic materials which are in a state of high internal strain, deliberately produced and designedly kept below the critical value at which mechanical rupture would occur.

Tests on Highly Non-Magnetic Stainless Steels for Use in the Construction of Weights. F. A. Gould.

(Journal of Scientific Instruments, 1946, vol. 23, June, pp. 124-127). In connection with the use of stainless steel weights, tests have been made at the National Physical Laboratory on different types of stainless austenitic steel to ascertain to what extent they are non-magnetic. Several weights of the 18/8 type used in this country proved to be appreciably magnetic and a few were even found to be permanently magnetized to an appreciable extent upon receipt at the Laboratory. Some other types of austenitic steel exhibited low permeability and retentivity, and rigorous tests, including severe cold-rolling, were made on three promising types. So far as non-magnetic requirements are concerned, austenitic steel is available which is far superior to the 18/8 type and is even better than much commercial brass. Details of permeability and retentivity values are given.

The Physical Properties of a Series of Steels. Part II. The Physics Division of the National Physical Laboratory. (Iron and Steel Institute, 1946, this Journal, Section I). The subject of the paper is a series of twenty-two steels, comprising eight carbon, eight alloy, and six high-alloy steels. The present account concerns work carried out on these steels subsequent to the publication of the first report. (See Iron and Steel Institute Special Report No. 24, p. 215).

Specific-heat measurements have been extended so that data are available up to about 1300° C. on all steels, a new method being developed for measurements above 900° C. Determinations of the coefficients of expansion of fourteen steels have been made, completing the series of steels up to about 1000° C., but excluding the steel of eutectoid composition. Electrical-resistivity measurements have been extended on all steels up to 1300° C. and measurements have been made of thermal conductivity of a 0.8% carbon steel (steel 7), up to 1000° C. and of a 13% manganese steel (steel 13) up to 850° C.

In addition, the report includes the results of a detailed examination of the effect of heat-treatment on the electrical resistivity and thermal conductivity of the 13% manganese steel and a note on the estimation of the thermal conductivity of steels from electrical-resistivity data.

Influence of Stress on Creep Failure. W. Stegfried. (Sulzer Technical Review: Iron and Coal Trades Review, 1946, vol. 152, June 14, p. 1072). The theories advanced by Rosenhain and Ewen, Thum and Richard, and Thielemann to account for creep failures are reviewed. The logical evaluation of the conceptions developed by Rosenhain and Ewen allows not only various phenomena to be explained which hitherto could not be interpreted, but it also furnishes a basis for determining the risk of failure with creep in a three-dimensional system of stress.

High Temperature Alloys. N. J. Grant. (Iron Age, 1946, vol. 157, May 23, pp. 42-48; May 30, pp. 50-56; June 6, pp. 77-80; June 20, pp. 60-63). This is a report on three years' intensive research work at the Massachusetts Institute of Technology on heat-resisting high-strength steels. The work had two main objects, first, to develop alloys for gas turbine construction to resist temperatures up to

1500° F., and secondly, to discover the effects of nitrogen and carbon on certain nickel-chromium-cobalt-iron alloys. Tables showing the composition and properties of many alloys are presented. The optimum carbon content of the nickel-chromium-cobalt-iron alloys was found to be 1.00-1.20%; in this system the high carbon content improved the strength but lowered the ductility. In the cobalt-chromium-molybdenum alloys the addition of carbon greatly increased the strength with no appreciable loss in the hot-ductility.

Cobalt-Base High Temperature Alloys. L. E. Browne. (Steel, 1946, vol. 118, May 27, pp. 88-91, 132). The properties of cobalt-nickel alloys are presented and discussed. These alloys, which were on the secret list during the war, were developed for such applications as gas turbines and superchargers.

Stress-Rupture Characteristics of Various Steels in Steam at 1200° F. J. T. Agnew, G. A. Hawkins, and H. L. Solberg. (Transactions of the American Society of Mechanical Engineers, 1946, vol. 68, May, pp. 309-314). Small specimens of a low-carbon steel, a 0.50%-molybdenum steel, three chromium-molybdenum steels, a 12%-chromium steel, two chromium-nickel steels, and a chromium-molybdenum-titanium steel were placed in a steam reaction chamber at 1200° F. and stressed in tension for periods of from 10 to 7700 hr. Data are presented on time to rupture, elongation, reduction in area, depth of scale, effect of type of flow, and type and angle of fracture. A straight-line relationship was obtained on plotting stress against time using logarithmic scales.

Report on Behavior of Ferritic Steels at Low Temperatures. Parts I. and II. H. W. Gillett and F. T. McGuire. (American Society for Testing Materials, 1945, Dec.). An extensive investigation was carried out under a contract between the War Production Board and the University of Kentucky to obtain and correlate data on the behaviour at low temperatures of commercial National Emergency and S.A.E. steels. The results are discussed in Part I. and the test data in the form of tables, curves, and micrographs are presented in Part II.

Thermal Characteristics, Microstructures and Physical Properties of Some Low and Medium Alloyed Cast Steels. W. L. Meinhart. (Iron Age, 1946, vol. 157, June 27, pp. 44-54). The effects of alloying elements on the transformation, hardenability, and microstructure of a number of cast steels cooled from 1832° F. at rates of 90° and 5.8° F. per min. were studied. The alloying elements were nickel, chromium, and molybdenum—the low-alloy steels containing not more than 1% of each, and the medium-alloy steels not more than 5.5%. The transformations were followed by dilatometer readings. The low-alloy steels could be classed in three groups: (a) Steels with no suppressed transformation on rapid or slow cooling; this caused low hardness and high ductility; (b) steels with suppressed transformation on rapid cooling, but not with slow cooling; an example was the 0.5%-molybdenum low-manganese steel; and (c) steels with suppressed transformations on slow cooling, which resulted in hardness values of about Vickers 300. The medium-alloy cast steels,

such as the 5%-chromium 0.5%-molybdenum 0.30%-carbon steels, have suppressed transformations even with a slow cooling rate of 5.8° F./min., which results in hardness values up to about Vickers 500.

Intermediate Manganese Steels. G. P. Contractor and J. S. Vatchagandhy. (Journal of Scientific and Industrial Research: Iron and Steel, 1946, vol. 19, July, pp. 427-429). An investigation of the properties of cast steels containing 1.35% to 1.65% of manganese with additions of up to 0.22% of vanadium is described. Vanadium improved the yield strength more than the tensile strength; it also improved the ductility slightly. The beneficial effect was observed when small amounts (0.08-0.12%) of vanadium were present and larger additions caused no further improvement.

Training Spark Testers. E. W. Lundahl. (Iron Age, 1946, vol. 158, July 18, pp. 65-67). An instruction programme is outlined for training men to determine the amount of carbon in steel by the spark test and to recognize the sparking characteristics of silicon, sulphur, phosphorus, molybdenum, nickel, and chromium in alloy steels.

Super Alloys for High Temperature Service. H. A. Knight. (Materials and Methods, 1946, vol. 23, June, pp. 1557-1563). Some of the heat-resisting alloy steels developed in the United States for use in turbines and jet aero-engines are discussed.

Chromium-Vanadium Carburizing Steel "6120." F. F. Franklin. (Materials and Methods, 1946, vol. 23, June, pp. 1564-1566). The properties of the 0.70-0.90%-chromium 0.10%-vanadium steel to specification A6120 of the American Iron and Steel Institute are discussed. This is a modification of steel S.A.E. 6120, the former being higher in manganese and hardenable to a greater depth.

Cast Iron in Contemporary Building and Engineering. J. G. Pearce. (Royal Society of Arts: Metallurgia, 1946, vol. 33, Apr., pp. 311-312). The structure and range of properties which can be obtained in cast iron by a combination of the art of the founder and the science of the metallurgist are discussed and its manufacture and uses are described.

Modern Cast Irons. A. E. McRae Smith. (Journal of the Institution of Production Engineers, 1946, vol. 25, Aug., pp. 217-227). A brief survey is presented of the properties of modern cast irons available to the production engineer today.

Impact Forging Improves Physical Properties. R. E. W. Harrison. (Machinist, 1946, vol. 90, July 20, pp. 624-626). Tables and curves are presented which show the improvements in the physical properties of plain carbon and alloy steels which are obtained by forging rolled billets.

High Strength Screws from Low Carbon Steel. G. F. Meyer. (Wire and Wire Products, 1946, vol. 21, Mar., pp. 225-227). Some particulars are given of the strength and hardness which can be obtained in cold-headed 0.18-0.23%-carbon steel screws after heat-treatment.

Advantages of High Strength Steel as Reinforcement for Concrete. L. J. Mensch. (Engineering Journal, 1946, vol. 29, Apr., pp. 234-239, 246). Data on the strength of concrete reinforced with various grades of steel are presented and the advantages of using high-tensile steel are discussed.

The History and Metallurgy of the Steam Locomotive. E. D. Connor. (Australian Institute of Metals: Australasian Engineer, 1946, May 7, pp. 65-71). The history of the development of the steam locomotive is reviewed and particulars are given of the analyses and properties of the steels now used in the construction of Australian locomotives.

Metallurgy and the Development of the High-Speed Diesel Engine. C. C. Hodgson. (Sheffield Metallurgical Association: Metallurgia, 1946, vol. 34, June, pp. 69-76). The design of Diesel engines and the metallurgical requirements of its components are discussed and information on the properties of the alloys used in their construction is given.

The Design and Production of Japanese Military Aircraft. A. P. West. (Journal of the Royal Aeronautical Society, 1946, vol. 50, July, pp. 526-549). An account is given of the stage of development of military aircraft attained in Japan. Airframe design is dealt with primarily. An appendix contains detailed information on metallic materials used in Japanese aircraft, their chemical composition, physical properties, and heat-treatment.

The Problem of Choice of Steel for Mechanical Construction. J. M. Dehalu. (Revue Universelle des Mines, 1941, vol. 84, No. 11, pp. 338-342). A brief discussion is given of the factors which should influence the choice of a steel for a given application. These include the fatigue strength, the wear and impact-resistance, and the machinability.

METALLOGRAPHY AND CONSTITUTION

(Continued from pp. 60 A-61 A)

Physical Metallurgy in Australia. A. F. Dunbar. (Australian Institute of Metals: Australasian Engineer, 1946, May 7, pp. 53-59). In this presidential address to the Australian Institute of Metals an account is given of the steps leading to the formation of the Institute in 1941, the work it has already done, and that which it hopes to do. The facilities for training metallurgists in Australia are also dealt with.

A Simple Fast Metallographic Polishing Method. R. B. McCauley, jun., and L. F. Mondolfo. (Materials

and Methods, 1946, vol. 23, June, pp. 1583-1586). A polishing technique suitable for several non-ferrous metals and alloys, and for cast iron, is described. After a flat has been made by grinding, filing, turning, or planing, the specimen is washed and then buffed against a wheel at least 1 in. thick made of discs of unbleached muslin from 8 to 12 in. in dia. A buffing paste containing alumina seems to be the best. Speeds between 3000 and 6000 r.p.m. can be used. Heavy pressure is applied at first and the specimen is

then turned 180° for the final polishing at low pressure. For buffing cast iron 7 to 10 min. is required.

The Grain Size of Austenitic Steel. J. Margulies. (*Revue Universelle des Mines*, 1941, vol. 84, No. 11, pp. 327-337). A general review is given of the factors which determine the grain size of austenite and the normality or abnormality of a steel. A bibliography of 39 references is appended.

Iron-Nitrogen, Iron-Carbon and Iron-Carbon-Nitrogen Interstitial Alloys; Their Occurrence in Tempered

Martensite. K. H. Jack. (*Nature*, 1946, vol. 158, July 13, pp. 60-61). It has been observed that when martensitic steel is tempered at 200° C. a fine dispersion of hexagonal Fe₃N is produced with no trace of cementite. At above 300° C. the reaction product is cementite; further, Fe₃N formed at 200° C. is transformed to cementite by heating at 350° C. The iron-nitrogen, iron-carbon and iron-carbon-nitrogen systems are examined and an explanation of the above observations is offered.

CORROSION OF IRON AND STEEL

(Continued from pp. 61 A-62 A)

The Corrosion and Protection of Iron and Steel. G. Tolley. (*Journal of the Birmingham Metallurgical Society*, 1945, vol. 25, June, pp. 81-113). A broad survey of some of the practical methods of combating the corrosion of iron and steel is attempted. Work on low-alloy steels has shown that increased corrosion resistance can be obtained by the addition of almost insignificant amounts of common metals. Specifications in painting procedure could result in a 50% increase in the efficient life of the paint. The use of synthetic-resin media in paints promises good results, and the direct bonding of plastics to metal may yet be widely used.

A Theory of the Mechanism of Rusting of Low Alloy Steels in the Atmosphere. H. R. Copson. (*Proceedings of the American Society for Testing Materials*, 1945, vol. 45, pp. 554-580). The results of exposure tests on low-alloy steel in industrial and marine atmospheres are presented together with analyses of samples of rust. In industrial atmospheres, copper and nickel in steel render the sulphate corrosion products more soluble by forming complex basic sulphates. On mild steel, sulphates in the rust are relatively soluble and promote corrosion but are washed away by rain. On alloy steels the sulphates are less soluble so that corrosion is slower, but less sulphate is washed away and more accumulates in the rust; the percentage of sulphates in the rust increases as loss-in-weight decreases.

A Study of Corrosion Control with Sodium Hexametaphosphate. P. E. Pallo. (*Journal of the American Water Works Association*, 1946, vol. 38, Apr., pp. 499-510). The influence of the rate of flow on the corrosion of ¾-in. black steel tubes by water treated with sodium hexametaphosphate was investigated and compared with the corrosion caused by untreated water. The corrosion of tubes carrying treated water is materially affected by the type of corrosion product formed at the various rates of flow. The phosphate dose of 2 p.p.m. did not prevent the removal of metal at any of the rates of flow applied, namely, 0.05, 0.27, 1.35, and 5.40 gal./min. The rate of corrosion increased with increasing rates of flow up to a critical rate of flow, above which the rate of corrosion fell to a low value. The rate of tuberculation also increased with increasing rates of flow up to a critical flow, after which the rate of formation of friction-producing products was materially reduced.

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Corrosion Resistance of Stainless Steels. J. M. Margolin, C. M. Sachnovitch, and P. I. Jusvinskaya. (*Iron Age*, 1946, vol. 157, May 23, pp. 50-55). An investigation is described in which specimens of six 13%-chromium steels with carbon contents in the 0.09-1.00% range were packed in solid decarburizing agents and heated to determine whether the decarburized surface would improve the corrosion resistance of the steel. The most effective decarburizing agent tested was MgCO₃. Corrosion tests in 10% nitric acid showed that the resistance of the high-carbon chromium steels was increased and became equal to that of the low-carbon chromium steels after 24 hr. treatment at 1920° F. in a 30/70 mixture of iron ore and MgCO₃.

Passivation of Stainless Steel. E. M. Mahla and N. A. Nielsen. (*Electrochemical Society*, Apr., 1946, Preprint No. 27). The strength and stability of passive films produced on stainless steel by various passivating treatments have been evaluated. In addition, electron diffraction has been applied to the study of passivated stainless steel surfaces and of bulk oxide films. Test data are presented which show that no passivation treatment confers lasting protection to stainless steel immersed in media which corrode the unpassivated metal. Bulk oxides produced by chemical or air-oxidation on 18/8 stainless steel were found to consist chiefly of Cr₂O₃ with no nickel oxide and little iron oxide present. The bulk oxides formed by air-oxidation on straight chromium-iron alloys consisted of FeO, Fe₃O₄, Fe₂O₃, and mixtures of these.

The Effect of Stabilizing and Stress Relief Heat Treatment upon Welded 18/8 Stainless Steel. W. G. Hubbell. (*Steel Processing*, 1946, vol. 32, Mar., pp. 181-186). Tests are described in which the formation of carbides in stabilized and unstabilized stainless steel was examined with a view to finding a method of increasing the service life of stainless steel aero-engine exhaust manifolds. A small beneficial effect was conferred on the corrosion resistance of stainless steels 321 and 347, stabilized with titanium and columbium respectively, by a stress-relieving treatment at 1650° F. for 30 min.

Permeability and Corrosion in Protective Coatings. D. F. Siddall. (*Corrosion*, 1946, vol. 11, June, pp. 78-84). The physical aspects of permeability, films formed from polymers, protective coatings, and the mechanism of film formation are discussed.

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A Note on the Effect of Tinsplate and of Lacquered Surfaces on the Oxidative Deterioration of Butterfat. C. H. Lea. (*Journal of the Society of Chemical Industry*, 1946, vol. 65, May, pp. 136-138). Little difference was observed in the storage life of butterfat when packed in sealed tinsplate and in lacquered containers. Dispersed as very thin films of the order of 0.02-0.06 mm. in thickness, butterfat was considerably less stable on a tinsplate surface than on lacquered blackplate.

Prevention of Condensate Well Corrosion by Chemical Treatment in the Erath Field. W. D. Yale. (*Corrosion*, 1946, vol. 11, June, pp. 85-94). A report is presented on the severe corrosion of steel tubes used in oil wells near Erath (Southern Louisiana) and the methods employed to prevent it. Injections of sodium dichromate into the well water were effective in preventing the corrosion.

Corrosion in the Water Industry. H. A. Price. (*Corrosion*, 1946, vol. 11, June, pp. 95-100). Problems connected with the corrosion of pipe lines and fittings which have confronted the Department of Water and Power in Los Angeles are reviewed.

Some Corrosion Problems Encountered in Steam Plant Operations. J. A. Keeth. (*Corrosion*, 1946, vol. 11, June, pp. 101-123). Experiences in dealing with corrosion problems on a boiler plant at Kansas City power station are reported.

Installation and Protection of Underground Gas Distribution Systems with Pipe-Line Enamel. P. D. Mellon. (*Corrosion*, 1946, vol. 11, June, pp. 124-132). A description is given of the methods employed in Alberta for enamelling the outside of gas pipes from 1 in. to 6 in. in dia. Details are given of the hinged troughs and containers which have been specially designed to enclose pipe fittings to act as containers for liquid enamel.

Rust Preventive Oils. G. P. Pilz and F. F. Farley. (*Industrial and Engineering Chemistry*, 1946, vol. 38, June, pp. 601-609). The value of films of mineral oils in preventing the corrosion of steel sheet for short periods between manufacturing processes was studied by measuring "contact angles." When a drop of distilled water rests on a horizontal steel panel coated with a film of oil the contact angle is the acute angle between the horizontal surface of the oil and a tangent to the surface of the drop at its periphery. An instrument for measuring this angle and the conditions for measuring it are described. Contact angles for a number of oils, some containing organic addition agents, were measured and a relationship was established between the contact angle and the rust-prevention properties of the oil in tests in a humidity cabinet.

The Effectiveness of Paint in Suppressing Galvanic Corrosion. G. W. Seagren, G. H. Young, and F. L. LaQue. (*Corrosion*, 1946, vol. 11, June, pp. 67-77). A report is presented on the results of corrosion tests in which copper and steel plates were bolted together to form the following systems of couples: (a) bare steel to bare copper; (b) bare steel and painted copper; (c) painted steel and bare copper; and (d) painted steel and painted copper. Five paint schemes were employed and the pairs of plates were suspended in flowing sea water. A second series of tests were

made to determine the corrosion rate of bare panels coupled to imperfectly coated copper cathodes.

A Variable Cycle Alternate Immersion Corrosion Testing Machine. C. H. Mahoney, A. L. Tarr, and K. A. Skeie. (*Proceedings of the American Society for Testing Materials*, 1945, vol. 45, pp. 719-721). An illustrated description is given of a machine for corrosion tests with which 48 specimens at a time can be dipped into and raised out of separate glass containers which are heated in a thermostatically controlled bath. The cycle of immersion and drying periods can be accurately controlled.

Corrosion of Steel by Gaseous Chlorine. G. Heine-mann, F. G. Garrison, and P. A. Haber. (*Industrial and Engineering Chemistry*, 1946, vol. 38, May, pp. 497-499). A study was made of the rate of corrosion and the ignition temperature of steel sheet exposed in dry chlorine gas for periods of 12 to 480 min. at temperatures in the 77-251° C. range. The rate of corrosion gradually increased as the temperature was raised to 248° C., whilst at 251° C. there was a very rapid increase in the rate for exposures of less than 30 min. After 30 min. at 251° C. the specimens ignited.

External Corrosion of Furnace-Wall Tubes : I.—History and Occurrence. W. T. Reid, R. C. Corey, and B. J. Cross. (*Transactions of the American Society of Mechanical Engineers*, 1945, vol. 67, pp. 279-288). Since 1942 many large power-station boiler furnaces fired with pulverized coal and removing the ash as molten slag have experienced external corrosion in the furnace-wall tubes. This report gives the results of the preliminary study of the occurrence of external corrosion, sixteen furnaces being examined. The corrosion was found to occur when the temperature of the tube metal was in the normal range for boiler furnaces, usually not exceeding 700° F., with maximum temperatures below 900° F. The deposits in the corrosion areas were of two types, one having an appearance of bluish-white porcelain enamel and consisting principally of sodium and potassium sulphates in complex form. The second type was iridescent blue or black, was insoluble in water, sometimes contained significant amounts of carbon, and consisted primarily of iron sulphide. The first type of deposit was made the subject of a special investigation (see next abstract).

External Corrosion of Furnace-Wall Tubes : II.—Significance of Sulphate Deposits and Sulphur Trioxide in Corrosion Mechanism. R. C. Corey, B. J. Cross and W. T. Reid. (*Transactions of the American Society of Mechanical Engineers*, 1945, vol. 67, pp. 289-302). The results of the laboratory investigation of the corrosive products referred to in the preceding abstract proved that the external corrosion of furnace-wall tubes is the result of the combined action on the tube surface of alkali-metal sulphate deposits and sulphur trioxide. The absence of either of these materials effectively prevents corrosion.

Electron Diffraction and Electron Microscope Study of Oxide Films Formed on Metals and Alloys at Moderate Temperatures. R. T. Phelps, E. A. Gulbransen, and J. W. Hickman. (*Industrial and Engineering Chemistry, Analytical Edition*, 1946,

vol. 18, June, pp. 391-400). The process of the oxidation of metals has been studied by electron diffraction and electron microscopy using oxide films stripped by procedures suggested by U. R. Evans and his co-workers. The metals studied were chromium, cobalt, copper, iron, molybdenum, nickel,

aluminium, columbium and tungsten. The electron micrographs and electron diffraction patterns are presented and discussed. The oxide films are shown to consist of small oxide crystals ranging in size from 100 to 2500 Å.

BOOK NOTICES

(Continued from pp. 64 A-66 A)

"*Dana's System of Mineralogy.*" Seventh Edition entirely rewritten and greatly enlarged. By C. Palache, H. Berman and C. Frondel. Vol. 1. "*Elements, Sulfides, Sulfosalts, Oxides.*" 8vo. pp. xiii + 834. Illustrated. New York, N.Y. 1944: John Wiley and Sons, Inc.; London: Chapman and Hall, Ltd. (Price £3).

The sixth edition of this work made its appearance as far back as 1892. Since that time vast changes have affected the science of mineralogy, and the new edition will be found to be essentially a new work.

The principal changes found necessary in the seventh edition are as follows: A new mineral classification based on crystal chemistry; a new elastic series of classification numbers for species; revised morphological elements based on the structural unit cell; a new form of presentation of the crystallographic data; introduction of data derived from X-ray crystallography; revision of specific gravities based on new observations; introduction of the optical characters of the opaque minerals; a new chemical treatment of species, with generalized formulæ for types, discussion of group relations, and a sharper definition of varieties; a new method of treating minerals that form a so-called series, that is, describing a series as if it were a single-species description; expansion and annotation of the reference section to include sources of data, transformation formulæ, lists of rare forms, general literature, and a statement of controversial questions requiring elucidation.

BOLKHOVITINOV, N. F. "*Metallurgy and Heat Treatment of Steel.*" Moscow, 1946: State Publishers of Technical-Scientific Books on Metallurgy. (In Russian).

One of the interesting features in this work is a useful list of recent Russian books on metallurgical subjects, including three of the author's own: (a) *Metallography and Heat-Treatment* (1933); (b) *Organizing a Works' Laboratory in Tractor Manufacture* (1935); (c) *Grain Size and Properties of Steel* (1943). In view of the present difficulty in getting up-to-date Russian text-books, it is at least something to know that they exist. Another valuable feature is the large number of tabulated data and specifications of Russian steels used for specific purposes, including tractor manufacture, in which the author is particularly interested. More generally, the book may be said to be a model of conciseness, for within the comparatively short compass of just over 300 pages Prof. Bolkhovitinov has succeeded in compressing a really wonderful amount of information, including a very large number of tables, curves, isothermal transformation diagrams, and photomicrographs.

The thirteen sections into which the book is divided

treat respectively: (1) Physico-chemical principles of metallurgy, including particularly plastic deformation and creep; (2) theory of alloys; (3) iron-carbon alloys; (4) carbon steels, especially steels for cutting tools, instruments, and cold stampings; (5) grey and malleable cast irons; (6) heat-treatment (or hot-working) of steels and cast irons in theory and practice, including ageing; (7) cementation, nitriding, cyaniding, and "aluminizing," i.e., heating the article up to 1050-1100° C. for 10-16 hr. in a powdered compact of ferro-aluminium 49%, aluminium oxide (Al₂O₃) 49%, and ammonium chloride 2%; (8) constructional alloy steels, including a comparison of Russian with American specifications; (9) industrial uses and hot-working of constructional steels, with particular reference to gears, crankshafts and axles, tractor parts, and agricultural machinery; (10) tool steels, including both carbon and alloy steels, high-speed steels, and hard alloys of the carbide type, with notes on casting or shaping the hard alloys; (11) steels and alloys with special physical and chemical properties, such as hard and soft magnet steels and alloys, alloys having a high ohmic resistance, steels with normal coefficient of linear expansion, wear-resistant steels, non-rusting and heat-resistant steels; (12) coloured alloys of copper, aluminium, magnesium, babbitt metal, alloys for pressure moulding or casting; (13) test methods, including mechanical, physical, thermal, metallographic tests, and the organization of a works laboratory.

In the section on constructional alloy steels the author points out that manganese steels are much more widely used in the Soviet Union than in the United States since supplies of that element in the latter are very much less than in Russia. On pages 172 and 173 he lists a large number of these steels containing up to 1.20% of manganese, together with silicon, chromium, and nickel, the nickel content in some cases being up to 4.60% and the chromium up to 1.75%, whilst the silicon is fairly constant at 0.15-0.30%. In some cases other elements are present, i.e., vanadium, molybdenum, tungsten, or aluminium. Traces of sulphur up to 0.05% and of phosphorus up to 0.04% are included.

The section on fine-engineering or tool steels contains further tables of composition of the standard marks or types, with varying content of carbon and manganese, whilst the following maximum limits are assigned: Silicon 0.35%, sulphur 0.04%, phosphorus 0.04%, chromium 0.30%, and nickel 0.25%. This is the U series of steels.

In a country like Russia where the mechanization of farming is developing on a huge scale, the importance of suitable steels for tractors and agricultural machinery generally cannot well be over-emphasized. Prof. Bolkhovitinov is fully aware of this, and in both the present work and those of earlier date he has devoted special attention to the subject.

W. G. Cass.

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(Continued from p. 42 A)

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ORES—MINING AND TREATMENT

(Continued from p. 17 A-18 A)

Technical Report on the Ruhr Coalfield. (British Intelligence Objectives Sub-Committee, 1946, vol. 1, Final Report No. 394: H.M. Stationery Office). A comprehensive account of the technical mining methods employed in the Ruhr coalfield is given, and recommendations are made regarding the possible application of some of these methods in Great Britain.

Mineral Exploration and the Outlook for Metal Supplies. G. F. Laycock. (Institution of Mining and Metallurgy: Engineer, 1946, vol. 182, July 5, pp. 10-11; July 12, pp. 38-39). The extent to which ores are being mined is related to the world's consumption of metals, and the vital need for more intensive mineral exploration in the world to-day is stressed. The following methods of prospecting are reviewed: (a) Aerial reconnaissance; (b) surface prospecting; (c) geological survey and mapping; (d) geophysical and geochemical methods; (e) diamond drilling; and (f) exploration by means of sub-surface workings.

Determinations of the Magnetic Susceptibility of Ores and Rocks from Swedish Iron Ore Deposits. S. Werner. (Jernkontorets Annaler, 1946, vol. 130, No. 7, pp. 253-272). (In Swedish). The paper is an abridged version of the author's report on magnetic-susceptibility and specific-gravity determinations of 525 samples of ore and rock from twenty-seven Swedish mines and ore deposits. The full report appeared in the Yearbook of the Swedish Geological

Survey, 1945, Series C, No. 472. The magnetometric method used was that of E. Thellier. Formulae are developed for the demagnetization factor of cylindrical samples and the volume-susceptibility κ . The magnetite determines the susceptibility of ores and rocks containing more than a small percentage of magnetite. A relationship was found between the susceptibility, the magnetite content, and the susceptibility of pure magnetite. In the skarn-bearing, calcareous, and quartzitic iron ores the susceptibility of the magnetite showed little variation. There were, on the other hand, considerable fluctuations in the case of apatite iron ores and high-manganese iron ores.

Present Problems in Our Iron and Steel Industry. Part I. Conditioning and Preparing the Blast-Furnace Burden—Crushing, Screening, and Sintering the Minerals. A. G. Lefebvre. (Association des Ingénieurs de la Faculté Polytechnique de Mons, 1945, No. 93). The preparation of ore for blast-furnaces and its distribution in the furnace are considered, and detailed descriptions are given of machinery and plant for crushing, screening, and sintering ore.

Iron Ore Preparation in Germany. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 592: H.M. Stationery Office). Descriptions are given of the following methods of beneficiating iron ore which are employed in Germany: (1) Crushing and screening; (2) wet-concentrating; (3) sintering; (4) nodulizing; (5) briquetting; and (6) the Krupp-Renn process.

FUEL

(Continued from pp. 67 A-69 A)

Automatic Control. J. E. O'Brien. (Society of Instrument Technology: Iron and Steel, 1946, vol. 19, Aug., pp. 459-469). The effect of the design of boiler auxiliaries on the choice and performance of automatic controlling instruments for boilers is dealt with. The items considered include dampers, and the control of fan-motor speed, stoker speed, feed water, and steam temperature.

Coal-Driers. Büttner-Werke A.G., Uerdingen-Krefeld. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXXIII-17: H.M. Stationery Office). A short description is given of a turbine type of coal-drier in which the coal, fed at the top, passes downwards on a series of slotted horizontal metal discs mounted in a vertical cylindrical metal shell. Three fans circulate heated air or gas over the descending coal.

Coke-Oven Installation of Reichswerke A.G., Hermann Göring Werke at Watenstedt near Brunswick. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXXIII-37: H.M. Stationery Office). Detailed descriptions are given, together with operat-

ing data, on the eight batteries of coke-ovens at the Hermann Göring Werke, Watenstedt. There are three batteries each of Otto and Koppers ovens, and one battery each of Becker and Still ovens.

Nordstern Coke-Oven Plant, Gelsenkirchner Bergwerks A.G. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXXIII-40: H.M. Stationery Office). A description is given of the four batteries of Still ovens comprising the coke-oven plant at the works of Gelsenkirchner Bergwerks A.G.

F. Krupp A.G., Altendorfer Strasse, Essen. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXXIII-16: H.M. Stationery Office). An account is given of a visit made to the Krupp works, in the course of which information was obtained on their coking practice, their methods of coal blending and testing, and on gas purification.

Gelsenkirchner Bergwerke A.G. (G.B.A.G.), Rosastrasse, Essen, and Nordstern, Wanne Eickel. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXXIII-18: H.M. Stationery Office). Brief descriptions are given of the coke-oven plants

and practice at the works of the Gelsenkirchener Bergwerke A.G. An appendix gives an account of the effect of adding 5% of dried and finely-ground coke breeze to the coking coal used at the Hamborn plant.

Heinrich Koppers G.m.b.H., Moltke Strasse 29, Essen. (British Intelligence Objectives Sub-Committee, 1945, File No. XXXIII-39: H.M. Stationery Office). A brief report is presented of a visit to Heinrich Koppers G.m.b.H., which was made to obtain information on recent developments in coke-oven practice, methods of testing coal and coke, and gas purification.

Gasification of Lignite and Sub-bituminous Coal. Progress Report for 1944. V. F. Parry, D. C. Gernes, J. B. Goodman, E. O. Wagner, A. W. Koth, W. L. Patty, and E. C. Yeager. (United States Bureau of Mines, 1946, Report of Investigations No. 3901). Investigations have been carried out by the Bureau of Mines with the object of finding a commercial process for gasifying lignite from the large deposits in northern Dakota and using the gas to reduce the low-grade iron ores of Minnesota. This report gives an account of the work done on the

gasification of lignite in laboratory retorts, in Glover-West retorts, in a water-gas machine, and in the pilot plant at Golden, Colorado.

Distribution in the Gas Producer. H. L. Saunders and R. Wild. (Iron and Steel Institute, 1946, this Journal, Section I). The problem of distribution in the gas producer is studied, with the aid of small-scale sectional models, from two complementary aspects, namely the segregation of the fuel and the distribution of the air blast. The segregation of the fuel was recorded photographically and was also analysed by dividing the model producer into vertical compartments by means of metal strips introduced from the back. The effects of various modifications of materials and of producer design were examined, and methods of segregation control are described. The air blast associated with various types of solid segregation were examined qualitatively and assessed quantitatively by measuring the pressure drop between various points across the bottom of the bed and the atmosphere. A special technique was devised to determine the extent and location of the ash-bed. Some preliminary experiments on the combustion of coal in a simple model producer are described.

PRODUCTION OF IRON

(Continued from pp. 69 A-70 A)

Just West of Timpanogos—Geneva Works. (Freyn-Design, 1945, July, pp. 1-15). Illustrated descriptions are given of the blast-furnace plant, the ingot-mould foundry and the rolling-mills at the Geneva Steelworks, near Mount Timpanogos, Utah, which was built during the war years for the Defense Plant Corporation.

The Blast Furnace Process and Means of Control. T. L. Joseph. (American Institute of Mining and Metallurgical Engineers: Blast Furnace and Steel Plant, 1946, vol. 34, June, pp. 709-714; July, pp. 855-860, 880, 881). See p. 46 A.

The Combustion of Coke with Oxygen-Enriched Blast and Its Effect on Smelting. R. Durrer, P. Lwowycz, and B. Marincek. (Iron and Steel Institute, 1946, Translation Series, No. 286). This is an English translation of a paper which was published in Archiv für das Eisenhüttenwesen, 1943, vol. 16, Mar., pp. 329-332. (See Journ. I. and S.I., 1943, No. II., p. 104 A).

Smelting Iron Ore in the Electric Low-Shaft Furnace. M. A. Kassen. (Iron and Steel Institute, 1946, Translation Series, No. 285). This is an English translation of a paper which was published in Schweizer Archiv, 1945, vol. 11, Mar., pp. 87-93. (See Journ. I. and S.I., 1946, No. I., p. 38 A).

Desulphurization of Pig Iron with Soda in a Skimmer Ladle after the Mixer. J. Willems. (Iron and Steel Institute, 1946, Translation Series, No. 283). This is an English translation of Confidential Report No. 43, April, 1943, to the Verein Deutscher Eisenhüttenleute. An investigation is described the aim of which was to achieve better utilization of soda in desulphurization. It was found that a saving of 40-50% of

soda could be effected when desulphurizing in the skimmer ladle after leaving the mixer. The amount of sulphur in the slag increased with the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio and with the manganese content. The soda slag obtained could be used repeatedly. The high-sulphur slag formed in this way can be utilized for the production of sodium sulphate and for the treatment of crude phosphate.

Thermodynamic Properties of Ilmenite and Selective Reduction of Iron in Ilmenite. C. H. Shomate, B. F. Naylor, and F. S. Boericke. (United States Bureau of Mines, 1946, Report of Investigations No. 3864). Any process for recovering the iron in the titaniferous iron ores of the United States will involve reduction of the iron in ilmenite. Investigations have been carried out to determine the low-temperature specific heats and the entropy of ilmenite.

Small-Scale Tests of Selective Reduction of Iron in Titaniferous Iron Ores. R. J. O'Dea. (United States Bureau of Mines, 1946, Report of Investigations No. 3886). Small-scale tests of the selective reduction, by carbon in the presence of sodium carbonate, of Wyoming titaniferous iron ores, followed by wet magnetic separation, have shown that it is possible to obtain magnetic fractions containing 90-95% of iron and 1-3% of titania, and non-magnetic fractions containing 40-70% of titania.

The Metallurgical Research Program of the Bureau of Mines Relating to Iron and Steel. R. S. Dean. (United States Bureau of Mines, 1946, Report of Investigations No. 3920). The research work of the Bureau of Mines during the last 15 years has included extensive work on iron-ore concentration, agglomeration, reducibility of ores and agglomerates, direct

reduction of iron ores and concentrates by a wide variety of processes, special refining processes for iron, the production of pure manganese, chromium, and cobalt from low-grade ores by electrolytic processes, and the production of ferro-alloys from indigenous low-grade ores. The stage reached in each of these fields and the future programme of work is outlined in this report.

The Low-Temperature Gaseous Reduction of Magnetite Ore to Sponge Iron. O. G. Specht, jun., and C. A. Zapffe. (American Institute of Mining and Metallurgical Engineering, Technical Publication No. 1960 : Metals Technology, 1946, vol. 13, June). This paper is in three parts : (1) An exhaustive examination of all previous work on the low-temperature gaseous reduction of iron ores ; (2) experiments on the reduction of magnetite with hydrogen ; and (3) development of certain thermodynamic relationships in reduction. The following conclusions were reached concerning reduction with hydrogen : (1) With increasing temperature, the thermodynamic potential of reduction increases regularly and rapidly whether the material is Fe_3O_4 , FeO , or wüstite, and initial reduction rates increase correspondingly and regularly, indicating that the thermodynamic driving energy of the reduction reaction is the principal factor in initial stages. (2) Above 600°C ., these initial rates lag, causing a maximum for total reduction to occur at 600°C . It is assumed that the product, iron, forms a physically impermeable diaphragm surrounding the semi-reduced particles. Hydrogen, which can diffuse chemically through the iron diaphragm, encounters enclosed iron oxide and forms H_2O which is trapped under quasi-equilibrium pressures ; this reduces the driving energy of the reaction to zero and reduction temporarily stops. This is the cause of the "lagging" phenomenon at above 600°C . (3) Calculation of the total pressure of the trapped gas reveals its ability to burst the surrounding film. With high furnace pressures, the potential internal pressure rises rapidly to hundreds of pounds per square inch. Disruption of the metallic film destroys the metastable equilibrium conditions and permits the reduction to proceed. Thus, with reduction under pressure, the maximum rates of reduction occur at temperatures above 600°C . (4) The confusion in the literature on the effect of bed depth can be clarified on the basis of thermodynamic potentials and the principles of pressure in gas-metal equilibria. (5) Decreasing the particle size from 10 to 100 mesh always caused an increase in the rate of reduction in the experiments

reported, indicating that intraparticle fusion reduces the reduction rate more than interparticle sintering. The conclusions relating to reduction with carbon monoxide were : (a) With increasing temperature the thermodynamic potential also increases steadily, whether thermal dissociation of the gas occurs or not. (b) Unlike reduction with hydrogen, carbon monoxide reduction involves reducing, oxidizing, and carburizing propensities. There is an infinite series of points in a narrow region of the phase diagram where gas, graphite, carboniferous iron, and oxide of a fixed composition co-exist, and one point where gas, graphite, FeO , Fe_3O_4 , and carboniferous iron may co-exist ; at above a certain temperature and carbon pressure the reduction reaction becomes irreversible for any given furnace pressure. (c) Carbon, rather than carbon monoxide, is judged to be the active agent in reduction, at least after initial stages. (d) Graphitization becomes more likely the purer the incoming carbon monoxide.

A bibliography of 228 references is appended.

Powder Metallurgy. J. E. Newson. (Proceedings of the Institution of Mechanical Engineers, 1946, vol. 154, No. 2, pp. 208-213). After enumerating the advantages and limitations of powder metallurgy, the author describes the process and gives examples of its application.

Production of Electrolytic Iron Powder. H. V. Trask. (Metal Progress, 1946, vol. 50, Aug., pp. 279-282). A description is given of the electrolytic process which is to be used for the large-scale production of iron powder at a plant in course of construction at Painesville, Ohio. The anodes consist of plates of ingot iron and the cathodes are of stainless steel. An electrolyte with an iron-chloride base is used with a current density of about 25 amp./sq. ft. The power consumption is about 0.75 kW./hr./lb. of iron produced. The classifier, annealing plant, and grinding machinery are also briefly described.

German Naval Mining Relays and Moulded Powder Permanent Magnets. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 587 : H.M. Stationery Office). This is a report of a visit to German works to obtain particulars of the design of devices for exploding mines and particulars of the manufacture of permanent magnets of special shape. An appendix contains an English translation of a paper by H. Dehler on the manufacture and characteristics of pressed permanent magnets for which synthetic resin was used as the bonding material.

FOUNDRY PRACTICE

(Continued from pp. 70 A-71 A)

A Modern Mechanised Foundry. (Mechanical World, 1946, vol. 119, May 31, pp. 602-604). A description is given of the equipment and layout at the new foundry of E. Green and Son, Ltd., makers of Green's economisers.

Hot-Blast Cupola Design. E. Longden. (Institute of British Foundrymen : Foundry Trade Journal, 1946, vol. 79, Aug. 13, pp. 387-395 ; Aug. 22, pp.

421-430). The theory and practice of hot-blast cupola operation are considered, and the following hot-blast cupola systems are reviewed with diagrams and operating data : Griffin, Cameron, Schuermann, Frauenknecht, Zoller, Olivo, Moore, Longden, Dyer, Whiting, and Piwowarsky.

Cupola Melting of Cast Iron. D. J. Reese. (New England Foundry Conference : Foundry, 1946, vol.

74, July, pp. 92-93, 197-203). Recommendations are made on the operation of cupolas with 36, 42, and 48-in.-dia. hearths producing from 10 to 20 tons/day of grey iron.

Developments in the Malleable Iron Industry. C. F. Joseph. (American Foundrymen's Association: Foundry, 1946, vol. 74, July, pp. 105, 217-218). Recent improvements in the methods of making malleable iron castings in the United States are briefly reviewed.

50 Years of Progress in Foundry Steel Melting. A. W. Gregg. (American Foundryman, 1946, vol. 9, May, pp. 58-68). An historical account is given of the development of steel-melting processes and equipment in American steel foundries.

Wartime Developments in Steel Castings. G. Vernerholm. (Metal Progress, 1946, vol. 50, July, pp. 75-80). Progress in methods of making steel castings in the United States in the period 1940-1945 are reviewed. Ceramic glazes for mould-washes have been used for preventing the metal from penetrating the mould wall. Special methods of centrifugal casting have been developed and examples of these are described.

Properties and Testing of Bentonite. D. G. Beech and M. Francis. (British Pottery Research Association: Transactions of the British Ceramic Society, 1946, vol. 45, Apr., pp. 148-160). Bentonite is a naturally occurring substance, probably derived from volcanic ash, the composition of which may be represented roughly by the formula $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot x\text{H}_2\text{O}$, in which part of the alumina may be replaced by iron, lime, magnesia or alkalis. The value of x ranges from 1 to 16, the higher values being associated with considerable swelling of the material. The swelling properties depend to some extent on the nature of the exchangeable cations. The material is obtained commercially in a very fine state of division, which accounts in part for its power of forming moderately stable suspensions and its high exchange capacity. Various properties of bentonite suspensions are discussed, and methods of testing, based on the swelling properties of the material, are described.

The Bonding Action of Clays. Part II. Clays in Dry Molding Sands. R. E. Grim and F. L. Cuthbert. (Illinois University, 1946, Engineering Experiment Station Bulletin Series No. 362). Whereas Part I. of this report dealt with bonding clays in green sands (see Journ. I. and S.I., 1945, No. II., p. 159 A), Part II. is confined to dry sands. Data are presented showing the relation of dry compression strength to amount of tempering water for varying amounts of each type of clay. Sands bonded with halloysite or kaolinite clays are unique in that they develop greatly increased strength without much loss of water when rammed specimens are allowed to dry slowly. This "air-set strength" is different from green strength and dry strength and was not found in sands bonded with montmorillonite or illite clays. A theory of dry strength is presented based on the wedge-block concept of holding grains in place. Because of air-set strength and other properties of some clays, it is difficult, or for some clays impossible, to predict the strength of a partially dried mould from simple green- or dry-strength determinations.

Synthetic Foundry Sands with Cement as a Binder. K. Endell and W. Strassmann. (Iron and Steel Institute, 1946, Translation Series, No. 284). This is an English translation of a paper which was published in *Giesserei*, 1942, vol. 29, Oct. 16, pp. 349-356. (See Journ. I. and S.I., 1946, No. I., p. 20 A).

Synthetic Sand Practice. J. J. Marais. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 79, Aug. 22, pp. 413-417). The advantages and disadvantages of using synthetic moulding sands are discussed and reference is made to experience in South African foundries.

Gray Iron Foundry Sands. (American Foundryman, 1946, vol. 9, Apr., pp. 143-147). This is a report by the Sub-Committee on Physical Properties of Gray Iron Foundry Sands at Elevated Temperatures which was appointed by the American Foundrymen's Association. A description is given of a method for measuring the work required to remove the core from a test casting. The results obtained with it using different core-sand mixtures are presented and discussed.

Fineness Test of Molding Sand. Margaret Price and A. I. Krynsky. (Journal of Research of the National Bureau of Standards, 1946, vol. 36, June, pp. 521-541). An investigation was made to evaluate the merits of the regular pipette, the Andreasen pipette, and the hydrometer method of making determinations of the fineness of Albany and Lumberton moulding sands. Full details are given of the hydrometer method, which was found to be preferable.

Mechanized Casting of Soil Pipe and Fittings. P. Dwyer. (Foundry, 1946, vol. 74, June, pp. 110-112, 246-258; July, pp. 102-104, 214). An account is given of the sand-preparation plant and the casting equipment at a modern American foundry manufacturing drain-pipes, boiler sections and radiator castings.

Plaster, Plastics and Low Melting Point Metals in Patternmaking. H. Plucknett. (Proceedings of the Institute of British Foundrymen, 1944-1945, vol. 38, pp. B64-B67). The characteristics of the following patternmaking materials are reviewed: (1) Plaster of Paris; (2) cast stone; (3) low-melting-point alloys; (4) cast synthetic resin; and (5) metal-sprayed patterns.

Metal-Faced Pattern Equipment. A. N. Whipp. (Institute of British Foundrymen, 1946, vol. 79, July 18, pp. 299-300). Metal facings of sheet brass or mild steel are sometimes fixed to mahogany patterns to increase the life of the surfaces subjected to rough usage. Recommendations are made for carrying out this work.

Pressure Feeding Iron Castings. W. J. Bradley. (American Foundryman, 1946, vol. 9, May, pp. 51-54). Examples of the judicious use of risers for feeding heavy iron castings are described and illustrated.

Atmospheric and Washburn Risers. W. E. Jones. (American Foundryman, 1946, vol. 9, Mar., pp. 35-38). Examples are described of the use of blind risers containing graphite rods for feeding steel castings. Details of the Washburn riser and how to make it are also given. This riser has a relatively thin core,

which constricts the metal at the junction of the riser and casting.

Malleable Iron Foundry—Core Practice. E. We-lander. (American Foundryman, 1946, vol. 9, Apr., pp. 112–114). A brief description is given of the production of dry sand cores at a foundry producing malleable iron castings for agricultural machinery.

Malleable Core Making Practice. E. C. Zirzow. (American Foundryman, 1946, vol. 9, May, pp. 35–42). The selection of core sands, methods of testing them, and ovens for drying cores for malleable iron castings are discussed.

Steel Susceptibility to Hot-Tear Formation in Castings. N. B. Gelperin. (American Foundryman, 1946, vol. 9, Apr., pp. 161–163). Causes of hot tears in steel castings are discussed. It is suggested that the contraction during the δ - γ transformation is an

important contributory factor. The effect of alloying elements on this transformation are dealt with.

Internal and External Hot Tears. H. F. Bishop and H. F. Taylor. (Foundry, 1946, vol. 74, July, pp. 82–87, 218). The importance of distinguishing between internal and external hot tears in steel castings is stressed. Examples of each are described and X-ray photographs of the former are shown. External hot tears can be prevented by the judicious application of chills, or by using weak moulding sand, which enables the mould to collapse and thus relieves the shrinkage stresses.

Eliminating Casting Defects. P. Boutin. (American Foundryman, 1946, vol. 9, Mar., pp. 42–44). The manner in which gas pressure and the direction of the solidification of molten metal in moulds lead to the formation of defects in castings is explained.

PRODUCTION OF STEEL

(Continued from p. 71 A)

French Iron and Steel Survey. S. H. Kahn. (Iron and Steel, 1946, vol. 19, Aug., p. 480). Statistics are presented on the recovery in the French iron and steel industry which has taken place since the end of the war.

Developments in the German Iron and Steel Industry, Ruhr and Salzgitter Areas. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXXII-119: H.M. Stationery Office). This book comprises a number of reports on all aspects of the German iron and steel industry in the Ruhr and Salzgitter areas.

Electricity Supply for Heavy Industry. S. E. Monkhouse. (North-East Coast Institution of Engineers and Shipbuilders: Iron and Coal Trades Review, 1946, vol. 153, Aug. 23, pp. 317–318). The proportions in which electricity is disposed of to different industries on the North-East Coast, in particular to collieries and steelworks, and its efficiency for various purposes in these industries are considered.

A Statistical Method and Results of a Study of Factors Affecting Open Hearth Production Rate. A. P. Woods and C. R. Taylor. (American Institute of Mining and Metallurgical Engineers: Blast Furnace and Steel Plant, 1946, vol. 34, July, pp. 847–854, 897, 901). A statistical method of studying how the production rate of open-hearth steel furnaces is affected by changes in the charging practice and other conditions is explained. For this purpose the graphical method explained in M. Ezekiel's book "Methods of Correlation Analysis" is applied by plotting data obtained from sorting 1155 punched cards each representing one heat. The following variables were recorded on the cards and numerous graphs are presented showing the relationship between different pairs of variables: (1) Percentage of ore charged; (2) percentage of limestone; (3) percentage of first hot metal; (4) percentage of total hot metal; (5) total weight of charge; (6) weight of burned lime; (7) weight of feed ore; (8) pounds of scale per ton of hot metal; (9) sulphur content of hot metal; (10) sulphur from ladle analysis; (11) carbon from ladle analysis;

(12) charging time; (13) time from finish charging to first hot-metal addition; (14) time between first and second hot-metal additions; (15) time from last hot-metal addition to tapping; (16) oil consumption; (17) number of charging boxes used; (18) whether cold pig-iron was added; (19) hours per ton of steel produced; and (20) length of campaign.

The Influence of Port Design on Open-Hearth Furnace Flames. J. H. Chesters and M. W. Thring. (Iron and Steel Institute, 1946, Special Report No. 37). In 1945 The United Steel Companies, Ltd., formed an Open-Hearth Advisory Committee which was to make recommendations on the standardization of steel furnaces and on means of increasing the efficiency of the Companies' existing furnaces. To further this object it was decided, among other things, that the characteristics of the flame in the furnace should be investigated as thoroughly as possible and that the work should be done on three furnaces of different design, namely, an old design, a streamlined design, and a Maerz design. Important work has been done by the British Coal Utilisation Research Association on heat transmission from flames in open-hearth furnaces, and the Advisory Committee asked for, and obtained, the very valuable assistance of the Association in solving some of the problems which arose.

The foregoing is explained by A. Robinson in the first part of the Foreword to this Special Report. In the second part of the Foreword, D. T. A. Townend sets forth the steps which led to the design and construction, by M. W. Thring and R. H. Baulk with the co-operation of the members of the Heat Flow Meter Panel of B.C.U.R.A., of an instrument and ancillary equipment capable of measuring the amount of heat passing downwards to the stock in unit time per square foot of surface exposed in open-hearth steel furnaces.

A full account of the trials made with this equipment is presented in this Special Report which is divided into three Sections entitled "Design of the Experiments" (3 Parts), "The Experiments" (14 Parts), and

" Interpretation of the Results " (2 Parts). Abstracts of the papers follow.

Purpose and Plan of the Trials. J. H. Chesters and M. W. Thring. (Iron and Steel Institute, 1946, Special Report No. 37, Section I., Part 1, pp. 4-16). Although there has been no revolutionary change in open-hearth furnace design since Siemens patented his first furnace in 1861, there have been many improvements resulting in bigger furnaces, faster working and greater reliability. Lack of fundamental information regarding the combustion processes in the laboratory of the furnace makes it impossible to design an open-hearth furnace in the sense that a bridge is designed.

The purpose of the present trials was to obtain some of this information by studying the effect of different port designs on the combustion, and in particular on the internal heat flow. This in turn was to be correlated with output rates. Three furnaces of very different type were chosen in one melting shop and several closely controlled test casts made on each furnace to decide which type was the most efficient and why.

External factors, such as the gas and air flow, gas quality, preheat temperatures, gas pressures and metallurgical load were controlled (or recorded), and heat-flow meters, narrow-angle radiometers, roof pyrometers, &c., used to study the internal radiation. The flame location, velocity and stability, together with the rate of mixing of the gases, were studied by means of slow-motion cinematograph films and a multiple sampling probe inserted through the roof.

The various port designs already suggested are discussed in an Appendix to this Section.

The Variability of Furnace Performance. I. D. L. Boswell and M. W. Thring. (Iron and Steel Institute, 1946, Special Report No. 37, Section I., Part 2, pp. 17-24). In order to provide a background for the trial results, the weekly averages and the variabilities of the charging plus melting and refining times over about a year and a half on each of the three trial furnaces are calculated and presented as functions of the date, age of crown and checkers, steelmaking variables, fuel supply and other factors. It is shown that the variability is so large (80 min.) that reliable comparisons cannot be made between furnaces in normal operation unless data for at least sixty casts are available, but that when sufficient data are available there are consistent differences of an hour in the mean melting plus charging times between *S* furnace (fastest) and *H* furnace. Particulars of the furnaces *H*, *K*, and *S* are given in Part 1. *K* is only 20 min. slower than *S* on the melting plus charging time, but is as slow as *H* on the refining time, for which both are 20 min. slower than *S*. Evidence is given that, like the melting time, the charging time is probably largely dependent on the flame characteristics. Except when crown and checkers are old, the variability from cast to cast within the same week nearly equals the total variability, but both the variability and the means are found to increase significantly when the furnaces are old. None of the steelmaking variables showed a significant correlation with the melting plus charging time, whereas both the port area and the gas-supply

rate accounted for a significant part of the cast-to-cast variability. It is concluded that the flame radiating power is the major factor by which improvements in output can be expected, and an indication is found that metering the gas may be alone sufficient to produce an appreciable improvement.

Preliminary Heat-Flow-Meter Survey. R. H. Baulk and R. Walker. (Iron and Steel Institute, 1946, Special Report No. 37, Section I., Part 3, pp. 24-30). Preliminary experiments are described which throw light on the best conditions for the determination of the pattern of flame radiation in any one cast of an open-hearth furnace by means of the heat-flow meter; it is shown to be necessary to make careful allowance for variation in the general radiation with time when only one instrument is used, and it is decided that it is essential to use two instruments simultaneously in the main trials to allow for this effect. One trial is described in which the gas-flow rate was also recorded, and it is shown that a much better correlation of the downward heat flow is obtained with the gas quality than with the gas quantity.

General Arrangement of Instruments and Fittings. J. E. Doyle and G. Lomas. (Iron and Steel Institute, 1946, Special Report No. 37, Section II., Part 1, pp. 31-34). The installation and maintenance of the large number of instruments used in the trials are described. Records were kept of some forty variables, twenty-three of these being automatically recorded. Approximately thirty men were required to take readings and maintain equipment, apart from those operating the furnace. The measurements had to be carried out without any interference with production and hence careful planning was required.

The general layout of the instruments and the connections between these and the recorders are shown in a plan. Details are also given of the mounting, both of instruments and of the recorders on the panels. Most of the latter were attached to the furnace chimney in order to minimize vibration. Warning was given of reversals by means of a siren, while a system of coloured lights was used to indicate the direction of the flame in the furnace.

Producer-Gas and Air Metering. H. E. Dall and J. Pluck. (Iron and Steel Institute, 1946, Special Report No. 37, Section II., Part 2, pp. 35-38). Pressure economy and other considerations influenced the decision to use a fixed Venturi tube made from refractory concrete for the gas measurement, and a metal Venturi intake for the air measurement, both coupled to differential recorders of the Kent ring-balance type. A description is given of the method of construction adopted, and of the model tests made for determining the appropriate value of the flow coefficients. The gas Venturis were scoured with compressed-air jets operated for a few seconds at four-hourly intervals.

Pressure Distribution in the Trial Furnaces. F. A. Gray and J. Senior. (Iron and Steel Institute, 1946, Special Report No. 37, Section II., Part 3, pp. 38-44). The principal pressures of interest in connection with the trials were those in the gas and air uptakes and in the furnace laboratory. These determine the rates of gas and air flow in the system, but are in turn determined by pressures at points further from the labora-

tory. Records were therefore taken at eighteen different points in the system with a view to getting a complete picture of the resistances to gas flow. Most of the pressures were taken with Arkon recorders or inclined gauges, but the roof and stack pressures were recorded by means of Electroflo and Bristol equipment.

Results showed that the gas supply to one end was about 10% greater than that to the other end, owing to the asymmetrical introduction of the gas involving an additional flue for one end of the furnace. The general pressure distribution was similar for each of the furnaces. Data plotted for *H* furnace at Templeborough showed that the gas flow was roughly a linear function of the pressure behind the port over the range normally used (60–100% maximum). Further studies on the trial furnaces and on models are recommended.

Recording of the Calorific Value of the Producer Gas. G. Lomas and R. Mayorcas. (Iron and Steel Institute, 1946, Special Report No. 37, Section II., Part 4, pp. 44–48). The installation and performance of a recording calorimeter operating on hot dirty producer gas are described showing the usefulness and need for such an instrument. The recorder was calibrated against spot samples analysed chemically. The calibration showed an accuracy well within $\pm 5\%$. It is recommended that a record of the quality of the gas available to a particular furnace be transmitted to the melter's cabin so that a distinction between quality and quantity can readily be made by the melter.

Preheat Temperatures of Gas and Air. I. M. D. Halliday. (Iron and Steel Institute, 1946, Special Report No. 37, Section II., Part 5, pp. 48–67). Suction pyrometers were used to measure the preheat (and also the waste-gas) temperatures at stage level in each uptake on the trial furnaces. The preheats obtained on the *H*, *K*, and *S* furnaces at Templeborough have been compared and the factors affecting preheat analysed. The main conclusions reached may be summarized as follows: (1) The air preheats in *S* furnace averaged 70–100° C. less than in *H* and *K* furnaces. (2) The gas preheats were from 130° to 270° C. lower than the air preheats. (3) The preheat depends on the waste-gas temperature for the previous half-cycle of the reversal. (4) Reversal averages of waste-gas temperatures tend to rise during a cast. (5) Charging of cold material and air infiltration due to open doors tend to lower the waste-gas temperature and hence the preheat.

Roof Pyrometry. J. H. Chesters. (Iron and Steel Institute, 1946, Special Report No. 37, Section II., Part 6, pp. 67–72). Since silica roofs are found to drip at 1680° C., and the final bath temperature generally exceeds 1600° C., roof pyrometry is considered essential to the maintenance of maximum output. Water-cooled total-radiation units sighted on the roof through holes in the back wall were found to give satisfactory results in the trial casts, though various improvements are suggested in the method of installation. The average error during the test runs amounted to only about 10° C.

Calibration by means of a disappearing-filament pyrometer is only satisfactory under black-body conditions, which generally exist only shortly after the completion of fettling and during the fully melted

period. Particular care must be taken to avoid temporary departure from black-body conditions during calibrating due to door openings, flame interference, &c.

Attempts to correlate roof temperature with gas flow, air flow, air/gas ratio, calorific value of the gas and preheat gave negative results, though big changes in gas flow had an obvious effect. The relationships are apparently rather complex and are partly hidden by the influence of such unmeasured factors as the "open-ness" of the bath.

Recording of Waste-Gas Analyses. J. R. Arthur, J. E. Doyle, and G. Lomas. (Iron and Steel Institute, 1946, Special Report No. 37, Section II., Part 7, pp. 72–76). The paper describes the method by which the waste-gas analyses were recorded. Descriptions are given of the instrument used and of the experiments which made possible its conversion to read CO_2/O_2 instead of CO_2/CO . Installation difficulties are described and a drawing showing the final layout which evades these is given.

The Control of Steelmaking. S. W. Pearson. (Iron and Steel Institute, 1946, Special Report No. 37, Section II., Part 8, pp. 76–84). A description is given of how a series of tests on three different furnaces was conducted. A measure of control was maintained through each part of the process, in order to standardize steelmaking for the purpose of experimental furnace testing. Whether the methods of control described are sufficient depends on the type of investigation taking place. If closer limits of control are demanded by the investigation, then it would be essential to use a more standard fuel and also to have identical steel specifications. The fuel quality, particularly on one test, was shown to be vitally important in isolating certain phenomena of flame characteristics.

The Performance of the Refractories in the Trial Furnaces. Y. K. Zea. (Iron and Steel Institute, 1946, Special Report No. 37, Section II., Part 9, pp. 84–97). Data concerning the general performance of the refractories of the three test furnaces are presented. Special attention is given to the furnace roofs, of which detailed records are shown in diagrammatic form. A survey is made of the factors affecting the life of open-hearth furnace roofs. These have been considered under three main headings, viz.: (1) Brick quality, (2) constructional or design factors, and (3) operational factors.

Laboratory and operational data covering twenty-nine roof campaigns on fourteen furnaces are given, and a study is made of their correlation with roof wear and ultimate roof life. Under the existing conditions the influence of brick quality and of constructional or design factors is less than that of the operational factors. The maintenance of flame direction has a marked effect on roof erosion. High roof temperatures and aged checkers both appear to increase the roof wear. Holiday-week shut-downs of furnaces are an important factor in reducing the average roof life.

Heat Loss through Water-Cooling of Ports and Doors. I. M. D. Halliday and A. R. Philip. (Iron and Steel Institute, 1946, Special Report No. 37, Section II., Part 10, pp. 97–106). The main purpose of water-cooling ports is to obtain better flame control. The

advantage of water-cooling doors and jambs is the reduction of air infiltration by the maintenance of the front wall against charger damage and the improvement of working conditions.

Of the three furnaces studied, two had water-cooled ports—one with a Maerz-type element, and the other with six water-cooling pipes as used in Venturi furnaces. The door and jamb cooling arrangements were similar for the two furnaces. The losses were measured by ordinary calorimetric methods involving the measurement of water flow and temperature rise. Details are given of the methods employed in overcoming certain complications, such as the addition of make-up water. The main conclusion is that the heat loss in the cooling water on the *K* and *S* furnaces at Templeborough amounts to about 10% and 6%, respectively, of the total heat input (both calorific and sensible) at the gas valve. This is divided between ports and doors into 3% and 7% for *K* furnace, and 2.5% and 3.5% for *S* furnace. The greater heat losses on *K* may be associated with the greater age of this furnace. The heat loss was found to vary continuously during reversals, being greatest at the exit end of the furnace. The cyclical temperature changes are similar to those obtained with the gases in the uptakes. It is suggested that a considerable number of super-refractory bricks could be economically employed in port ends, provided that they gave equal service to water-cooling.

The Measurement of Heat Flow in the Trial Furnaces. R. H. Baulk, J. J. Reilly, and R. Walker. (Iron and Steel Institute, 1946, Special Report No. 37, Section II., Part 11, pp. 106–117). Two heat-flow meters were used in all the trials. These were inserted through the three doors, and used to measure the downward heat flow at positions on the central axis of the surface and halfway towards the front. One heat-flow meter was kept at door No. 1 and the other one used at both doors 2 and 3. In the last four trials a twin-calorimeter heat-flow meter was used to measure in addition the upward radiation from the slag surface; in these trials and in the three on *K* furnace, use was made also of total-radiation pyrometers sighted through the flame at the back wall, and of a heat-flow meter built into the roof.

The heat-flow measurements are used for three purposes:

(1) The assessment of the grand mean heat flow from the flame for a whole cast (in Section III., Part 2, this is compared with the melting time). This is the most significant characteristic of a furnace.

(2) To determine the flame-radiation pattern ("mosaic") which indicates the length and width of the flame in each furnace. Any one furnace varies enormously in this respect according to the air- and gas-flow conditions, so that *H* furnace gave the longest flame in trials *H1*, *H2*, and *H3* and the shortest in *H4*, *H5*, and *H6*. One significant result which emerges is that the flame is narrower at the ingoing end on *S* furnace than on *H* or *K*.

(3) To assess the variations of downward heat flow during the period of measurement.

This assessment has shown, first, that the downward radiation at the ingoing end fluctuates independently of that over the rest of the furnace, whereas the middle and outgoing ends fluctuate together. This latter connection is, moreover, shown to be due rather to some persistent flame characteristic than to an overall change of furnace temperature. *The variation at the ingoing end within a reversal is accounted for (to the extent of 60–90%) by the variation in the sensible heat of the gas due to the cooling of the checkers, while the variation between reversals is not significantly different from the residual variation within a reversal after the sensible heat is allowed for.* The relation between downward heat flow and sensible heat within a reversal is such that an increase of 1 C.H.U./cu. ft. of combustion gas (equivalent to a change of 1° C. in air and gas preheat) is equivalent to an increase of downward heat flow of 5000 C.H.U./sq. ft.-hr. At the outgoing end there is no correlation with the sensible heat, and the variation between reversals is rather greater than that within reversals. Of the between-reversals variation, 33% is accounted for by the fluctuations in gas rate and a further 7% by measured fluctuations in gas quality. Owing to the known difficulties in measuring fluctuations in gas quality it is highly probable that a more detailed measurement of gas quality could account for considerably more of the total variation at the outgoing end. The relation with gas rate at the outgoing end is such that a 1% increase in gas rate gives about a 1½% increase in net heat flow. Broadly, therefore, the main causes of variation of flame radiation are the fuel- and air-input conditions and these causes are sufficient to account for so much variation that, if they could be kept at their optimum, the flame would be so powerful that a very significant reduction of furnace time would accrue.

There are four appendices to this paper. In the first R. L. Brown and F. Fereday attempt to assign the variability of the heat flow to specific causes. In the second R. H. Baulk and J. J. Reilly give details of the twin-calorimeter heat-flow meter used in the last four trials. In the third M. W. Thring describes the arrangement of the front-wall pyrometer, and in the fourth R. Mayorcas gives details of the continuous-flow water calorimeter used to measure the total upward heat flow from the steel and flame.

The Emissivity of Producer-Gas Flames in Open-Hearth Furnaces. R. Mayorcas. (Iron and Steel Institute, 1946, Special Report No. 37, Section II., Part 12, pp. 129–137). An account is given of laboratory and industrial experiments, carried out by several investigators, in which the radiation from luminous and non-luminous flames was measured. It is possible for two flames at different temperatures to radiate equal quantities of heat per unit volume, though the characteristics of the radiations would be different. For the complete characterization of a flame it is necessary to measure two of the three quantities: Total heat radiated, emissive power, gas temperatures. Methods of measuring gas temperatures with thermocouples have on the whole not been successful, since the high temperatures and gaseous conditions in industrial furnaces affect their accuracy. A study of the methods used by Schack, Schmidt, and

Sherman for measuring the emissivity of gases led to the development of the narrow-angle radiometer, a description of which is given together with the underlying theory. The experiments described include measurements of the radiation from several thicknesses of flame inside the furnace, and also some measurements taken right across the furnace, sighting the radiometer through a hole in the back wall on to a door directly opposite. It is concluded that the incoming end of the flame is strongly luminous, but conditions in the outgoing end show that the flame here is non-luminous. The curve obtained at the outgoing end agrees well with that of Hottel and Mangelsdorf for non-luminous radiation, and it is possible to make an estimate of the relative temperatures and emissivities of both ends of the flame. Spectrographic analysis shows the persistence of the sodium-vapour radiation throughout the flame, against a strong continuous spectrum in the incoming end, but against a faint background in the outgoing end. It is suggested that an attempt be made to use the sodium-line reversal method for measuring temperatures in industrial furnaces.

The Effect of Port Design on Gas-Air Mixing in the Open-Hearth Furnace. J. J. Reilly, R. Phillips, and D. Franklin. (Iron and Steel Institute, 1946, Special Report No. 37, Section II., Part 13, pp. 138-143). It is shown on theoretical grounds that an index of the gas-air mixing conditions (and therefore of the flame length) in an open-hearth furnace can be obtained by taking gas samples with water-cooled sampling probes at different heights in the flame. Some preliminary experiments in a glass tank led to the design of a multiple sampling probe with which samples could be taken simultaneously at four different heights over the bath. Experiments were made with such a probe in each of the three open-hearth steel furnaces of the trials, and it was found that, provided that suitable precautions were taken, a clear index of the relative mixing conditions could be obtained. A comparison of the three furnaces indicates that the best one is that which gives the shortest flame by good mixing in the lower half of the furnace, while at the same time it gives the greatest degree of horizontal stratification.

Cinematography of Open-Hearth Furnaces Flames. J. H. Chesters and A. R. Philip. (Iron and Steel Institute, 1946, Special Report No. 37, Section II., Part 14, pp. 143-150). Slow-motion cinematograph films taken with a Zeiss Ikon Movikon 16-mm. camera at one-thousandth of a second exposure provide valuable information regarding flame location, velocity, and stability. Ten shots were taken on each trial cast just before the fully melted stage. Five were taken with the flame going from left to right and five with it going from right to left. The first three shots were taken through the main doors in a direction perpendicular to the front wall; the fourth and fifth shots were oblique views of the incoming and exit ports. These latter were taken to show the stability of the incoming jet and the extent of "tailing" of the exit gases. Measurements of the films enabled the height of flame at each door, the flame "flap" and flame velocity to be determined. Most of the velocity values

were calculated for surges on top of the flame, but in the later tests strontium nitrate was introduced into the gas uptake and the speed at which the crimson coloration crossed the doors was determined.

S furnace showed the height, "surge," velocity, and the least tendency for the flame to lift between the first and second doors. *H* furnace had the greatest tendency to tailing of the exit gases.

General Results with Conclusions and Recommendations. J. H. Chesters and M. W. Thring. (Iron and Steel Institute, 1946, Special Report No. 37, Section III., Part 1, pp. 151-171). An attempt is made in this paper to give a self-contained summary of the trials. This is followed by an explanation of the main results, with conclusions as to the heating process in open-hearth furnaces. The paper concludes with recommendations for the design, operation, and testing of such furnaces.

In the trials the melting-plus-charging times were between 1 and 2 hr. shorter than during comparable non-trial casts, whereas little significant difference appeared in the final refining times. While part of the gain in melting time was due to the use of special materials in the trials, a large part can be attributed to an improvement in the heating power of the furnace, resulting from the use of instruments during the trial casts; in particular:

(1) A diminution of air infiltration achieved by roof pressure control. Thus, an increase of roof pressure of 0.03 in. W.G. can reduce the air infiltration from 50% of the producer-gas volume to a negligible amount.

(2) The use of the maximum gas quantity for a longer time, made possible by the close observation of roof temperature by recording pyrometers.

Where it is possible to adjust the air flow to the furnace over a sufficient range, the use of an air meter to obtain a gas/air ratio of 1/1.4 is also beneficial. The trials thus show that an increased heat flow to the charge, which is the primary factor governing melting rate, can be obtained not only by increasing the quantity of fuel burnt, but even more by increasing the theoretical combustion temperature. This depends on the CO_2 in the combustion gases (gas/air ratio) and upon the preheat. The importance of the latter factor is brought out by the fact that the heat flow at the ingoing end drops by 10-20% during each reversal owing to the fall in preheat.

Comparing the three furnaces during the trials, *S* furnace was found to be considerably quicker than *H* and *K* furnaces. *K* was working with old checkers, but evidence is given that it would not have been as quick as *S* even if the checkers had been new. The first three trials on *H* (*H*1, *H*2, *H*3) and on *S* (*S*1, *S*2, *S*3) were run with the correct gas/air ratio, and in these trials it was found that *S* furnace used 29% more fuel per ton of steel than *H*. The rapid melting rate of *S* furnace is mainly due to a very high flame radiation in this furnace (as measured with the heat-flow meter), and it is concluded that this high radiation is largely due to a high flame temperature resulting from (a) stratification in a vertical plane so that the excess air flows along the top of the flame, (b) the high gas

quantity, and possibly (c) better mixing in a horizontal plane, giving a short flame. It is suggested that the interval between completion of charging and the fully melted state is a critical one during which a maximum flame radiation is essential if the overall time is to be kept short.

In regard to furnace design, the use of a more elaborate system of gas and air passages which allow a very high heat input rate during the critical period, and the improvement of flame luminosity are recommended, but the most important point is to obtain a maximum flame temperature by reducing air infiltration and using a maximum preheat. The semi-Venturi port is the most promising of the three investigated, and a further improvement is proposed.

General Theory of Heat Transfer in the Open-Hearth Furnace. M. W. Thring. (Iron and Steel Institute, 1946, Special Report No. 37, Section III., Part 2, pp. 171-187). Evidence is given that the main factor accounting for variations of melting time, which, in the three 80-ton open-hearth furnaces investigated, varied between the limits of $10\frac{1}{2}$ and $5\frac{3}{4}$ hr., was the variation of the downward heat flow as measured with the heat-flow meter. The mean downward heat flow varied between values corresponding to black-body radiation at 1600°C . and 1700°C . The paper discusses quantitatively the separate influences of quantity, flame emissivity, theoretical flame temperature, and flame length in producing such variations in downward heat flow. An attempt is made to explain how the higher radiations are achieved without overheating the crown.

In Section II. the downward heat flow and roof temperatures resulting from any given flame temperature and emissivity are calculated. When the flame radiation is altered, the relation between the downward heat flow and roof temperature is found to be much the same whether this is effected by altering the temperature or by changing the emissivity; such difference as does exist is in the sense that a greater downward heat flow can be obtained with a given roof temperature by using a flame of low emissivity but high temperature. Where, however, insufficient heat is available to bring the roof temperature up to the safety limit, increase of emissivity (*e.g.*, by tar addition) is very desirable. In most furnaces the roof temperature represents a radiation equilibrium with the flame and charge, but the interposition of a cooler heat-absorbing layer can permit a higher heat transfer to the steel with given roof and slag temperatures.

In Section III. the flame temperature is calculated for various heat inputs and combustion conditions;

it is here assumed that the flame radiates uniformly over the whole bath, until it reaches a temperature at which its rate of heat loss by radiation balances its available heat. This calculation shows the great value of an improvement in the flame temperature by controlling the gas/air ratio or by increasing preheat as compared with an increase in fuel input.

In Section IV. the effect of shortening the flame by improving the mixing conditions is assessed by carrying out similar calculations but with the bath divided into three successive zones. These results may be summarized by saying that the heat transfer and thermal efficiency depend mainly on the working flame temperature and that, while this temperature is naturally dependent on the fuel consumption (particularly at the outgoing end), *it is much more easily and cheaply increased by increasing the sensible heat per unit volume of combustion gases*, whether this is done by increasing the preheat or by reducing the excess air in the radiating zone.

The markedly shorter melting times experienced in the *S* furnace at Templeborough are thus shown to be associated with the fact that the excess air passes along the top of the furnace so that the "theoretical" flame temperature is higher; the large gas quantity, however, also makes a significant contribution, and if the flame is in fact shorter in *S* than in *H* furnace, which is indicated, but not proved, by the heat-flow-meter and multiple-sampling-probe data, then the theory shows that this shortening will also play a part in increasing the downward heat flow in *S* furnace. The roof is not overheated, because the cooler layer above the flame cools it.

Finally, the conclusions as to the relative importance of gas quantity and theoretical flame temperature and as to the way in which these factors affect the net heat transfer at different points along the flame are shown to be in accord with the facts brought out in preceding papers in this Report.

Electrolytic Manganese in Low-Carbon Steel. Tests at the Stanley Works, Bridgeport, Conn. F. Sillers, jun., and R. T. C. Rasmussen. (United States Bureau of Mines, 1946, Report of Investigations No. 3911). This paper constitutes the third report of a series on the value of electrolytic manganese additions in place of ferromanganese in steelmaking processes (*see* Journ. I. and S.I., 1946, No. I., p. 21 A). It deals with the use of electrolytic manganese in making low-carbon rimming and killed steels. As a ladle addition for these steels, electrolytic manganese proved to be equal or superior to the ordinary grades of ferromanganese, but the price factor is against its use.

FORGING, STAMPING, AND DRAWING

(Continued from pp. 71 A-72 A)

The Modern Direct-Hydraulic System. F. H. Fowler. (Proceedings of The Institution of Mechanical Engineers, 1946, vol. 154, No. 2, pp. 178-189). The advent of the high-speed reciprocating ram pump has produced the modern direct-hydraulic system in which the press and pump form one self-contained unit.

The power to drive the pump is in direct proportion to the work done by the press, and the speed and pressure exerted by the press ram can be precisely controlled. The author considers that a saving of at least 75% in electric power can be made by conversion from the accumulator system to the direct-hydraulic system.

Indicator diagrams are reproduced to show the saving in power which can be achieved by the direct-hydraulic system. Many illustrations of direct-hydraulic presses are presented.

Railworthy Wheel-Making at Armco's Butler Steel Plant. (Steel, 1946, vol. 119, July 15, pp. 106-110, 146). An illustrated description is given of the forging, pressing, rolling, and heat-treatment processes in the manufacture of heavy wheels for rolling stock.

Forging High-Alloy Rounds with V-Type Dies. E. Ghrist. (Iron Age, 1946, vol. 158, Aug. 1, pp. 44-49). When forging square high-alloy steel billets between flat dies into rounds greater than 5 in. in dia. there is usually a high proportion of rejections because of rupture in the metal at the centre. A new technique is described and illustrated by which the billet is first forged between conventional flat dies into a square section. The anvil is then changed to a V-section die and the square billet, after reheating, is put in the die with one corner uppermost. By rotating the billet 90° each time it is forged into an octagonal section and approaches the diameter of the desired round. The sides of the square billet should be 3 in. longer than the desired diameter of the finished round.

Forging Die Design. J. Mueller. (Steel Processing, 1946, vol. 32, June, pp. 376-378). A 1000-ton coining press is briefly described and examples of the work which can be done in modern coining presses are given.

Manufacture of Steel Tubing by Hot Extrusion at

Mannesmann Röhrenwerke, Annen-Witten, Ruhr, Germany. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXVII-88: H.M. Stationery Office). A detailed description is given of the extrusion machinery and process used at one of the Mannesmann plants for making steel tubes. The process is suitable for tubes up to 3.6 in. in outside dia. with wall thicknesses in the 0.08-0.12 in. range in soft steel. The raw material consists of cold-sawn bar stock from 4.5 to 6.4 in. in dia., 12 in. long, depending on the size of tube desired.

Quality Control of Bolt and Nut Products at Sheffield Steel Corporation. H. W. Gronemeyer. (Steel Processing, 1946, vol. 32, June, pp. 359-362). The exacting system of inspection and testing in force at the works of an American firm making bolts and nuts is described.

Redesign Furthers Increased Use of Stampings. (Steel Processing, 1946, vol. 32, June, pp. 368-371). Improvements in the techniques of stamping, curling, and brazing have reduced the cost and improved the appearance of many metal articles. Several examples of such articles are described and illustrated.

Electrical Drives for Wire-Drawing Machines. G. P. F. Newlands. (Metropolitan Vickers Gazette, 1946, vol. 21, Apr., pp. 168-179). The power requirements of wire-drawing machines are explained and examples are described of electrical drives suitable for machines of different types.

ROLLING-MILL PRACTICE

(Continued from pp. 72 A-73 A)

First Report of the Rolling-Mill Research Sub-Committee of the Iron and Steel Industrial Research Council. (Iron and Steel Institute, 1946, Special Report No. 34). The Rolling Mill Committee of the Iron and Steel Industrial Research Council was formed in 1930 and was first concerned with factors determining the efficiency of rolling-mill operation. In 1936 and 1937 a series of conferences was called to examine the possibilities of research into the problems of plant design; these were attended by British rolling-mill-plant designers and managers, and scientists interested in allied problems. A Panel was appointed to inspect the experimental rolling mills available in Great Britain. This Panel reported that there was no experimental mill then available which would offer suitable facilities but, pending the provision of such a mill, it was recommended that: (a) The examination of the published literature on this subject, which had already been started, should be continued, (b) a survey should be made of the existing unpublished technical knowledge of rolling-mill operation, (c) a report should be submitted on the instruments available for rolling-mill research, and (d) investigations should be made at selected mills where certain facilities might be obtained for working on ferrous and non-ferrous metals. The Rolling-Mill Research Sub-Committee was formed to direct this work, and a full account of the progress made in carry-

ing out these recommendations is presented in this Special Report, which is divided into five Sections.

In the introduction (Section I.), E. C. Evans describes the steps, a summary of which is given above, which led to the formation of the Rolling-Mill Research Sub-Committee and briefly explains the contents of the Report.

The Panel's recommendation that the published literature should be surveyed has been carried out by L. R. Underwood who presents in Section II. a critical survey of the literature on rolling-mill research. This survey concludes with a summary setting out certain very definite primary problems in rolling-mill research which require further elucidation and proposals for a scheme of research involving: (1) Quantitative verification of von Karman's or other friction-hill theory of the pressure distribution between the roll and the material; (2) experimental determination of the natural resistance to flow, free from friction effects, for hot and cold rolling; (3) the investigation of the effect of front and back tension in cold rolling; (4) the investigation of the magnitude and effect of roll flattening; (5) subsidiary problems. The classified bibliography at the end of this section contains 184 references.

Section III., by H. Ford, contains a detailed description of the experimental rolling mill at the Metallurgical Department of the University of Sheffield and the equipment fitted to it to enable the work in

view to be carried out; this included Ward-Leonard control, regulating gear, coilers, and tensioning equipment. The special instruments for making the required measurements are also described. The experimental programme is well under way.

Mention is made in Section III. of the instrument which was developed for the measurement of roll-separating force. In Section IV., A. L. M. Douglas and H. Ford deal fully with the measurement of this force. They discuss the methods which have been used in the past and the reasons why the new method was developed. The circuits used in the new unit are

described and full details are presented of the pressure head, together with details of calibration tests.

In Section V., E. Orowan and K. J. Pascoe discuss methods of calculating the distribution of roll pressure over the arc of contact in hot flat rolling. For everyday computations in rolling-mill practice speed of calculation is often more important than high accuracy, so that approximate methods of computation are desirable. A simple approximate method of roll-load and torque calculation for hot flat rolling is explained in this section.

HEAT-TREATMENT

(Continued from pp. 73 A-74 A)

Salt Bath for Heat Treating 18-8. K. Whitcomb. (Metal Progress, 1946, vol. 50, Aug., pp. 294-298).
Salt Bath Treatment for 18-8 Stainless Steel. K. Whitcomb. (Steel Processing, 1946, vol. 32, May, pp. 317-322). A description is given of the development of a salt bath for treating aero-engine exhaust manifolds made of 18/8 stainless steel in order to relieve the stress set up by welding and to remove the welding flux. The results of tests with a number of commercial barium-chloride salts and with pure sodium carbonate are reported. A satisfactory procedure using sodium carbonate, which reduced the process time from 59 to 15 min., is described.

Carbon Rod Rectification. S. M. DePoy. (Steel, 1946, vol. 119, July 15, pp. 114-116). When high-speed steels are heat-treated in barium-chloride baths slight decarburization takes place at the surface of the tool; the amount increases with the age of the bath and it becomes serious unless the bath is "rectified." Data are presented which show that a graphite rod immersed in the bath keeps the decarburization of the tool steel at a negligible amount, and is more effective than silica additions. The life of the electrodes which heat the bath is also increased when a graphite rod is used.

Rectification of High Temperature Salt Baths. R. S. Burpo, jun. (Materials and Methods, 1946, vol. 24, July, pp. 109-111). The prevention of decarburization when tools are heat-treated in barium-chloride baths is discussed and experience gained in using graphite rods to rectify such baths is related.

Manufacture of Surgical Instruments. F. McKnight and J. C. Cowley. (Steel, 1946, vol. 119, Aug. 5, pp. 126-127, 170-174). The surgical-instrument industry is almost unique in that it combines modern machining and heat-treating methods with the hand craftsmanship of metalworkers. Steps in the manufacture of surgical scissors and forceps are outlined and described.

Determination of the Depth of Surface Decarburization in Rolled and Drawn Steel. H. Kjerrman. (Jernkontorets Annaler, 1946, vol. 130, No. 7, pp. 239-252). (In Swedish). As a preliminary to standardization the author has surveyed different methods of determining surface decarburization of steel. The best practical method is to measure the depth of the decarburized layer with a microscope on an etched cross-section. Three alternative definitions of the depth to be measured are given: (1) The depth of the ferrite, *i.e.*, in which the carbon content is practically nil; (2) the surface layer in which the structure may vary from 100% ferrite to 100% lamellar pearlite, *i.e.*, up to eutectoid composition; and (3) the layer in which the structure indicates a carbon content lower than the average carbon content of the steel. Examples of measurements in accordance with these three definitions are shown on micrographs.

Induction Heating. (Automobile Engineer, 1946, vol. 36, May, pp. 204-206). American developments in the heat-treatment of internal surfaces by induction heating are discussed.

WELDING AND CUTTING

(Continued from pp. 74 A-75 A)

The Spot Welding of Low Carbon Mild Steel Sheet. W. S. Simmie. (Sheet Metal Industries, 1946, vol. 23, Aug., pp. 1573-1577). Investigations are described the object of which was to determine the optimum values for (a) welding current, (b) pressure, (c) time of weld, and (d) forging time after welding, for the spot-welding of 16 S.W.G. mild steel sheet. The results indicate that the increase in weld strength obtained by allowing the test welds to age before testing occurs in both Bessemer and open-hearth low-carbon steel sheet. The rate of age-hardening increases rapidly in the first

seven days, after which any further increase is small. The welding time does not influence the age-hardening.

German Chain Industry. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 565: H.M. Stationery Office). A report on the capacity and processes used in the German chain industry is presented. Particular attention is given to the welding procedures.

Three-Phase Distribution and Electric Welding and Furnace Loads. A. Langley Morris. (Journal of the Institution of Electrical Engineers, 1946, vol. 93,

Part II., Aug., pp. 341-348). See Journ. I. and S.I., 1946, No. I., p. 78 A.

The Pressure Weldability of Iron. H. Esser. (Sheet Metal Industries, 1946, vol. 23, Aug., pp. 1578-1583). This is an English translation of a paper which appeared in *Archiv für das Eisenhüttenwesen*, 1930, vol. 4, Oct., pp. 199-206 (see Journ. I. and S.I., 1930, No. II., p. 553).

Mild Steel to Cast Iron. E. W. Harding. (Welding, 1946, vol. 14, Aug., pp. 356-359). An account is given of a method of welding a steel strip of 24 S.W.G. to a hot-plate casting for an electric cooker. A disc of 18 S.W.G. mild steel, $\frac{1}{4}$ in. in dia., was prepared with a slight projection in the centre. This was spot-welded to the steel strip. The strip was then resistance-welded to the casting between flat electrodes, sufficient pressure being exerted to force the disc into the casting.

Developments in Low Alloy Steels for Welding Construction. A. J. K. Honeyman and J. Erskine. (Metallurgia, 1946, vol. 34, July, pp. 133-139). A number of low-alloy steels of good weldability are reviewed. The Reeve weldability test is described and the effect of alloying with manganese, silicon, nickel, chromium, titanium, vanadium, and molybdenum on the welding properties is discussed.

Gray Iron Castings—Welding and Salvage. J. A. Griffin. (American Foundryman, 1946, vol. 9, Mar., pp. 16-23). Methods of repairing grey-iron castings by welding, brazing, soldering, and plugging are described with illustrated examples.

Oxygen Cutting. E. Seymour Semper. (Welding, 1946, vol. 14, July, pp. 329-334; Aug., pp. 360-364; Sept., pp. 403-410). The latest types of equipment and techniques for manual and machine oxy-acetylene cutting are reviewed.

PROPERTIES AND TESTS

(Continued from pp. 78 A-80 A)

Notch Brittleness and the Strength of Metals. E. Orowan. (Institution of Engineers and Shipbuilders in Scotland, 1945, Paper No. 1063). Theories relating to notch brittleness and the strength of metals are critically examined, the subject being dealt with under the following headings: (1) Mechanical testing and engineering design; (2) types of fracture; (3) molecular and technical strength; (4) experimental verification of the crack theory of brittle strength; (5) the fracture condition for brittle fracture; (6) ductile fracture; (7) the Ludvik theory of notch brittleness; (8) the plastic constraint factor of the ideal notch; (9) elastic superstrengthening as a possible cause of notch brittle fracture; (10) notch brittleness and velocity of crack propagation; (11) notch brittleness and low-temperature brittleness; (12) a criterion for the mechanism of brittle fracture; (13) Kuntze's "Cohesive Strength"; and (14) fatigue fracture.

The Effect of Rate of Strain on Mild Steel. R. P. Andrew. (Engineering, 1946, vol. 162, Aug. 23, pp. 171-172). Experiments to determine the effect of rate of strain on the ductility of mild steel are described. For the tests at high rates of strain the machine described by R. J. Lean and H. Quinney was used (see Journ. I. and S.I., 1937, No. II., p. 273 A). In the high speed tests, impact had very little effect upon the reduction in area, but there was a considerable difference between the reduction-in-area figures with and without a notch, the former being the smaller. The ultimate tensile strength showed a steady increase with increasing depth of notch. The ultimate tensile strength also increased with increasing rates of strain. Whilst the absorption-of-energy data showed a considerable fall with increasing notch depth, the values increased with increasing speed of testing. The appearance of the fractures confirmed that increased rates of strain do raise the tendency of a steel towards failure in a brittle manner.

The Limitations of Mechanical Test Results. J. N. Greenwood. (Australian Institute of Metals: Australasian Engineer, 1946—ii.

Asian Engineer, 1946, June 7, pp. 35-42). Limitations to the value of data obtained in tensile, Izod, and fatigue tests, as well as those due to sampling difficulties, are discussed.

50 Years of Progress in Cast Metals—Specifications. J. W. Bolton. (American Foundryman, 1946, vol. 9, Apr., pp. 98-102). The author traces the development of specifications for the foundry industry in the United States and their effect on quality control. He explains the relationship between the American Foundrymen's Association and the American Society for Testing Materials in issuing standards for products.

Non-Destructive Inspection of Castings. C. L. Frear and R. E. Lyons. (American Foundryman, 1946, vol. 9, Apr., pp. 120-133). A brief description is given of the following methods of testing castings: Visual inspection, sound or percussion tests, impact tests, pressure tests, radiographic examination, magnetic inspection, electrical conductivity tests, penetration tests, and supersonic tests. The advantages and disadvantages of each are outlined.

Cast Iron—Modulus of Elasticity. A. J. Herzig. (American Foundryman, 1946, vol. 9, Apr., pp. 134-135). A large number of stress-strain measurements in transverse bend tests were made and used to calculate elastic moduli for cast iron. The results were plotted against the content of graphitic carbon in each case. It is considered advisable to use data from transverse tests rather than the results of tensile tests.

Gray Cast Iron. H. H. Palmer. (Australian Institute of Metals: Australasian Engineer, 1946, June 7, pp. 80-84). Developments and improvements in the production and properties of grey cast iron are reviewed.

Supersonics in Metallurgy. (Metal Industry, 1946, vol. 69, Aug. 16, pp. 136-138). This article is based on a paper by N. Marinesco presented to the Centre de Perfectionnement Technique. It reviews progress made in the employment of supersonics in both the light and heavy engineering industries. The applica-

tions described include lowering of the solidification temperature of metals, tinning aluminium, modifying magnetic properties and increasing the chemical activity of metals.

Influence of the Gauge-Length and Shape of Test-Pieces upon the Elongation at Fracture. A. Krupkowski and J. Wantuchowski. (*Annales de l'Académie Polonaise des Sciences Techniques*, 1939-1945, vol. 7, pp. 10-40). A detailed study is made of the deformation of specimens in the tensile test and a formula is developed for the elongation of standard specimens. A nomograph is presented which simplifies the conversion of the elongation and reduction in area of a specimen of the standardized dimensions of one country to those standardized in another.

Verification of Tensile Testing Machines. W. Thompson. (*Metallurgia*, 1946, vol. 34, July, pp. 145-146). A comparatively simple method of checking the accuracy of tensile-testing machines, using a steel proving ring, is described.

The Electrical Measurement of Strain. S. C. Redshaw. (*Journal of the Royal Aeronautical Society*, 1946, vol. 50, Aug., pp. 568-602). The methods available for the electrical measurement of strain are comprehensively reviewed with particular reference to the recording instruments.

Use of Electric Resistivity Strain Gages over Long Periods of Time. G. P. Tschebotarioff. (*Proceedings of the Society for Experimental Stress Analysis*, 1946, vol. 3, No. 2, pp. 47-52). The precautions to be taken in the use of the SR-4 strain gauge over long periods of time are explained.

A Method of Effecting SR-4 Strain Gage Operation under Water. E. L. Kimble. (*Proceedings of the Society for Experimental Stress Analysis*, 1946, vol. 3, No. 2, pp. 53-54).

Improved Techniques and Devices for Stress Analysis with Resistance Wire Gages. W. V. Bassett, Helen Cromwell, and W. E. Wooster. (*Proceedings of the Society for Experimental Stress Analysis*, 1946, vol. 3, No. 2, pp. 76-88).

A Review of Some Mechanical Failures of Steel Plant Machine Equipment. S. W. Poole and R. J. Johnson. (*Proceedings of the Society for Experimental Stress Analysis*, 1946, vol. 3, No. 2, pp. 61-75). Detailed descriptions are given of the methods applied to discover the causes of failure of the following parts of steel plant machinery: (1) A Diesel locomotive crankshaft; (2) a rolling-mill pinion; (3) the gear wheel on the main hoisting drum of a crane; (4) several shafts used to drive a large saw for cutting hot bars and billets; (5) the rolls of a cold rolling mill; and (6) several failures associated with welding.

Fatigue Failures in Aircraft. K. Arnstein. (*Proceedings of the Society for Experimental Stress Analysis*, 1946, vol. 3, No. 2, pp. 124-130). A description is given of an apparatus and procedure for fatigue-testing structural members such as girders, tubes, and spars under axial pulsating or alternating loads at rates ranging from 2400 to 6000 cycles/min.

Fatigue Tests of Some Manufactured Parts. O. J. Horger. (*Proceedings of the Society for Experimental Stress Analysis*, 1946, vol. 3, No. 2, pp. 133-136). The fatigue testing of automobile rear axle

shafts, connecting rods, and gudgeon pins is described.

Effect of Understressing and Overstressing in Fatigue. J. B. Kommers. (*Proceedings of the Society for Experimental Stress Analysis*, 1946, vol. 3, No. 2, pp. 137-141). The results of several series of fatigue tests are presented by stress/number-of-cycles curves. The endurance limit of cast iron was increased by about 16% by understressing at low stresses from 6500 to 8000 lb./sq. in., but when the understress was close to the endurance limit the increase was greater and amounted to about 31%. The results of overstressing tests showed that the effect on the endurance life depended, in some cases at least, on the sequence in which the two overstresses were applied. When the high stress was applied first there was a bad effect on the subsequent endurance life; when the low stress was applied first there was generally a good effect on the endurance life.

The Metallurgical Phase of Fatigue Failures. H. W. McQuaid. (*Proceedings of the Society for Experimental Stress Analysis*, 1946, vol. 3, No. 2, pp. 142-148). The causes are traced of a wide variety of fatigue failures of parts. These include gear teeth, a joint in a tool for drilling in an oil field, and a drill pipe which rotated under a high pressure of water. The examples show that tensile and fatigue test data are insufficient criteria on which to base the selection of a steel for a particular service.

Amount Gained in Fatigue Strength of Machine Parts by Using a Material of Higher Tensile Strength. R. E. Peterson. (*Proceedings of the Society for Experimental Stress Analysis*, 1946, vol. 3, No. 2, pp. 149-151). Fatigue and tensile test data on plain and notched specimens are presented with the object of showing the extent of the gain in fatigue strength obtained by using a steel of higher tensile strength. In the case of a shaft with a notch of $\frac{1}{4}$ -in. radius, the gain in the fatigue strength between steels of 75,000 and 150,000 lb./sq. in. becomes less with increasing diameter of the shaft, or increasing depth of notch. When the notch has a radius of $\frac{1}{8}$ in. the improvement in fatigue strength is very much larger.

Some Aspects of Fatigue in Diesel Engine Parts. C. G. A. Rosen and R. King. (*Proceedings of the Society for Experimental Stress Analysis*, 1946, vol. 3, No. 2, pp. 152-160).

Cracking in Service of 0.5% Molybdenum Steel Steam Piping. (*British Electrical and Allied Industries Research Association, Technical Report J/T141: Engineer*, 1946, vol. 182, Aug. 16, pp. 149-150). Sub-committee J/E of the British Electrical and Allied Industries Research Association has surveyed cases of cracking which have occurred in 0.5%-molybdenum steel steam piping and in this report makes recommendations which will considerably reduce the risk of this cracking. Further investigations on the causes are proceeding.

Metallurgical Control in Automobile and Aero-Engine Production. S. W. Porter. (*Australian Institute of Metals: Australasian Engineer*, 1946, June 7, pp. 65-69). The practical application of metallurgical reasoning to material control in automobile and aero-engine production is reviewed. The

limitations of testing in each stage of production are pointed out.

Statistical Control Applied to Wrench Manufacture. F. J. Robbins. (Metal Progress, 1946, vol. 50, Aug., pp. 287-290). Examples are given of the application of statistical control to the results of surface inspection, hardness tests, and torque tests in the production of spanners so as to ensure that a high proportion of the output complies with the specifications.

Factors for the Calculation of Hardenability. I. R. Kramer, S. Siegel, and J. G. Brooks. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 2029: Metals Technology, 1946, vol. 13, June). Grossmann's method of calculating the hardenability of a steel from its composition and grain-size is examined, especially with regard to the need for correction factors in the light of data now available for manganese, silicon, and certain other elements. The correction for grain-size depends on the deoxidation practice, aluminium-killed steels requiring a greater correction than silicon-killed steels. The correction-factor curves for carbon, manganese, and silicon were derived and formed a balanced system. Grossmann's multiplying-factor principle was found to be valid, but the principle that alloying elements act independently must be modified when two or more elements forming stable carbides are present. When both chromium and molybdenum are present, their combined effect is less than that predicted by the product of their individual factors.

Microhardness Testing of Fine Wire and Small Parts. G. E. Shubrooks. (Wire and Wire Products, 1946, vol. 21, July, pp. 515-518, 548, 549). The Tukon hardness testing instrument, utilizing the Knoop indenter, is described, and examples of its application for testing fine wire and small parts are given.

A Critical Survey of Hardness Tests. A. F. Dunbar. (Australian Institute of Metals: Australasian Engineer, 1946, June 7, pp. 46-57). Hardness tests, particularly those of more recent origin, are critically examined.

On the Connection between the Magnetization and Hysteresis Curves of Polycrystalline Ferromagnetic Bodies. N. Popzov and L. Tchernikova. (Journal of Physics, 1946, vol. 10, No. 1, pp. 85-91). The connection between the magnetization and hysteresis curves of magnetic soft polycrystalline ferromagnetic bodies, having a small constant of magnetic anisotropy, is studied.

A Small-Scale Creep-Testing Unit. G. T. Harris. (Metallurgia, 1946, vol. 34, July, pp. 129-132). A detailed description is given of a creep-testing machine which was designed to meet the following requirements: It had to be relatively inexpensive to construct and maintain, occupy a minimum of space, use a small test-piece, apply stresses up to 30 tons/sq. in., and be capable of making strain measurements as small as 0.001% of the gauge length. An automatic strain-time recorder and an extensometer for more refined measurements were also developed for this machine. Some results obtained with it are also presented.

Use of Stainless Steel as a Structural Material in Jet-Propelled Aircraft. G. Brewer. (Metal Progress,

1946, vol. 50, July, pp. 84-88). Reasons are given for the use of stainless steel sheets in the construction of the rear two-thirds of the fuselage of jet-propelled aircraft, and data on the resistance to buckling of stainless steel panels are given.

Superalloys for High Temperature Service in Gas Turbines and Jet Engines. F. S. Badger, H. C. Cross, C. T. Evans, jun., R. Franks, R. B. Johnson, N. L. Mochel, and G. Mohling. (Metal Progress, 1946, vol. 50, July, pp. 97-122). This is a verbatim report of a round-table discussion at the American Society for Metals' National Metal Congress and Exposition held at Cleveland, Ohio, on February 5, 1946. Much information is given on the composition and properties of heat-resisting alloys.

Metallurgical Development of Materials for Turbo-superchargers and Aircraft Gas Turbines. W. L. Badger. (Iron Age, 1946, vol. 158, July 25, pp. 40-45; Aug. 1, pp. 60-66). Particulars are given of some of the ferrous and non-ferrous alloys used in the manufacture of supercharger parts. The ferrous alloys include Timken Alloy (a 16/25/6 chromium-nickel-molybdenum steel) and several stainless steels.

Some Recent Trends in Alloy Steels. R. S. Archer. (Society of Automotive Engineers: Steel Processing, 1946, vol. 32, June, pp. 363-367, 371, 388-389). Several recent American papers on hardenability, the effects of changes in the temperature of testing and in the rate at which the load is applied, and the effects of different microstructures on the strength properties of steel are discussed, and the manner in which wartime conditions influenced the development of new S.A.E. and National Emergency steels is also considered.

Grain-Growth Inhibitors in Steel. J. W. Halley. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 2030: Metals Technology, 1946, vol. 13, June). An investigation of the effectiveness of aluminium, titanium, and zirconium in preventing grain growth in steel is reported. The three elements differ in the manner and degree in which they inhibit grain growth. Aluminium is most effective when 0.028% is present as acid-soluble aluminium. The simple relation between the titanium content and the grain-coarsening temperature indicates that the mechanism of the inhibition by titanium is much less complex than that when aluminium is used. Zirconium is the least effective of the three elements. The improvement in notched-bar impact strength at low temperatures caused by the addition of these elements is due more to the formation of alloys than to refinement of the grain.

Copper and the Steel Casting—An Alloy for Post-war Consideration. H. F. Taylor, H. F. Bishop, and R. C. Wayne. (American Foundryman, 1946, vol. 9, May, pp. 72-83). The addition of copper to steel increases the yield and tensile strengths and the yield-strength/tensile-strength ratio without materially affecting the ductility. With additions of more than about 0.6% of copper, steel high in manganese and silicon can be precipitation-hardened without quenching in a liquid. Because a supersaturated solution of copper in ferrite is obtained by very slow and uniform cooling, sections as large as 8 in. can be hardened

throughout by tempering after normalizing. If a cast copper-bearing steel contains less than 0.20% of carbon it will be readily weldable. Copper-bearing steels are more resistant to scaling during heat-treatment than plain carbon or carbon-molybdenum steels.

Manganese Steel. (Mining Journal, 1946, vol. 227, Aug. 31, pp. 692-694). The properties, structure, machining, welding, and applications of manganese steel are briefly reviewed.

Developments in Tool, Die and Special Steels. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXIX-29). A general summary of the development in Germany during the war of tool, die, and special steels is presented.

German Tool and Special Steel Industry. (Combined Intelligence Objectives Sub-Committee, 1945, File No. XXXI-26). Tables are presented showing the analyses and trade names of the tool and die steels manufactured in Germany during the war.

Use of Cemented Carbides in Steel Processing. F. Hennig. (Steel Processing, 1946, vol. 32, June, pp. 379-382). Details are given of the physical and mechanical properties of a cemented carbide called Kennametal together with descriptions of many of its applications such as dies, rolls for rolling nickel strip, thrust bearings, and cutting tools.

A Precipitation-Hardening Stainless Steel of the 18 per Cent Chromium, 8 per Cent Nickel Type. R. Smith, E. H. Wyche, and W. W. Gorr. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 2006: Metals Technology, 1946, vol. 13, June). An extensive investigation of the properties of the steel called "Stainless W" is reported. It is a precipitation-hardening ferritic stainless steel of the 18/8 type which can be heat-treated in all wrought and cast forms to give a range of mechanical properties similar to that of the cold-worked austenitic 18/8 steels.

METALLOGRAPHY AND CONSTITUTION

(Continued from pp. 80 A-81 A)

Metallographic Etchant to Distinguish Oxidation in Steel. A. M. Hall. (Metal Progress, 1946, vol. 50, July, pp. 92-96). A new etching agent for studying the oxidation of welds in steel is described and micrographs of etched specimens are presented and discussed. The solution consists of 10 g. each of KMnO_4 , NaOH , and Na_2CO_3 , plus 4 g. of $\text{K}_2\text{Cr}_2\text{O}_7$, dissolved in 100 c.c. distilled water. The solution is heated to boiling and the specimen is immersed with the polished face upward. Boiling is continued until the surface develops a brownish-blue to purple-blue tint; this takes from 10 to 40 min., the time decreasing with increasing carbon or carbide content.

The Electrolytic Polishing of Metals. P. Schafmeister and K. Volk. (Iron and Steel Institute, 1946, Translation Series, No. 288). This is an English translation of a paper which was published in *Archiv für das Eisenhüttenwesen*, 1941, vol. 15, Nov., pp. 243-246. (See Journ. I. and S.I., 1942, No. II., p. 34 A).

The Technique of Gamma Radiography. R. Halmshaw. (Engineering, 1946, vol. 162, Aug. 23, pp. 169-170). A description is given of some practical problems in gamma-radiography, and the following variable factors which influence the correct exposure are discussed: (1) Source to film distance; (2) specimen thickness; (3) strength of source; (4) type of film; (5) type of intensifying screens; and (6) development technique.

Precise Measurements and Inspection by Stereoscopic Radiography. B. J. De Simone. (Metal Progress, 1946, vol. 50, July, pp. 71-74). A description is given of a stereoscopic radiographic method of measuring the wall thickness of hollow steel propeller blades for aeroplanes and of determining the exact position of minor defects below the surface of the material.

The Sigma Phase in Certain High-Chromium Steels. F. B. Foley. (Metallurgia, 1946, vol. 34, July, pp. 139-145). The occurrence of a hard, brittle, and non-magnetic constituent, termed the "sigma phase"

in certain high-chromium steels is discussed and the literature, particularly the work of A. J. Bradley and H. J. Goldschmidt (see Journ. I. and S.I., 1941, No. II., p. 273 P), is reviewed. The detection of this phase by X-ray diffraction, magnetic analysis, and etching is also dealt with. This phase appears to be the intermetallic compound FeCr in which the chromium, in iron-chromium alloys richer in iron than 50 atomic-%, may be replaced by iron atoms.

The Martensite Transformation. A. R. Troiano and A. B. Greninger. (Metal Progress, 1946, vol. 50, Aug., pp. 303-307). The following characteristics of the martensite transformation are discussed: (1) The transformation is without diffusion of elements, and involves no change in chemical composition; (2) it progresses only while the specimen is cooling and ceases if the fall in temperature is interrupted; (3) the temperature range of martensite formation is characteristic of a given alloy and cannot be lowered by increasing the cooling velocity; (4) all recorded martensite transformations have been shown to be reversible below the equilibrium temperature, except those in plain carbon and relatively low-alloy steels; (5) all metastable phases which complete the martensite transformation at below room temperature will also produce martensite upon deformation at room temperature; (6) martensite is probably never in a condition of real equilibrium, although many martensitic structures may persist indefinitely at or near room temperature; (7) martensite always has a greater hardness than the parent solid solution from which it is formed; and (8) the martensite plates are always parallel to a given crystallographic plane of the parent lattice.

The Temperature Range of Martensite Formation. R. A. Grange and H. M. Stewart. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1996: Metals Technology, 1946, vol. 13, June). See p. 37 A.

The Relationship between Transformation at Constant Temperature and Transformation during Cooling. G. K. Manning and C. H. Lorig. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 2014 : Metals Technology, 1946, vol. 13, June). The relationship between the beginning of transformation during continuous cooling and the beginning of transformation at constant temperature of five steels containing carbon 0.30% and chromium in the 0.51% to 2.40% range was studied. Specimens of two of the steels were quenched in two temperature steps rather than in the single step commonly used in

studying isothermal transformation. It was found that from the A_{c3} temperature down to about 1130° F. the time spent at a given temperature divided by the time required for beginning isothermal transformation at that temperature may be regarded as a fraction of the nucleation period, and that nucleation began when the sum of such fractions was unity. An expression was developed for calculating the temperature at which transformation begins during cooling. On checking the validity of the expression by data from end-quenched bars, the experimental and the calculated results differed appreciably for two of the five steels.

ANALYSIS

(Continued from pp. 62 A-64 A)

Photometric Analysis. J. Parina, jun. (Steel, 1946, vol. 118, June 17, pp. 110-111, 137-140). A description is given of the Cenco-Sheard-Sanford photometer for making rapid determinations of the light passed through coloured solutions. Its unusual features are the use of optical filters to limit closely the wavelength of the light source to that of the absorption band of the test solution, and the use of a light source the intensity of which remains constant in spite of fluctuations in the line voltage.

Application of Thioglycolic Acid to the Spectrophotometric Determination of Iron in Ores. J. P. Mehlig and M. J. Shepherd, jun. (Chemist Analyst, 1946, vol. 35, Feb., pp. 8-14). Application has been made to the determination of iron in iron ores of the spectrophotometric method which depends upon reducing the iron with hydroxylamine hydrochloride and measuring the light transmittancy at 535 $m\mu$ of the coloured solution produced by thioglycolic acid in ammoniacal solution. The results agree closely with those obtained by the dichromate titrimetric method and give further evidence that it is possible to determine macroconstituents spectrophotometrically. The few diverse ions which interfere are not normally present in iron ores.

Metallurgical Analysis. J. Sanders. (Iron and Steel, 1946, vol. 19, July, pp. 423-425). The substances in general use as dessicants in chemical analysis are reviewed with notes on their action of dehydration, appropriate properties, and relative efficiencies.

Micro Spot Test for Cobalt. C. D'E. Barker. (Chemist Analyst, 1946, vol. 35, May, p. 38). In the detection of cobalt with Vogel's reaction, the sensitivity of the test is increased by using sodium thio-

sulphate to prevent the interference of ferric iron. The test procedure is described.

Sulphur Determination. (Iron and Steel, 1946, vol. 19, July, p. 426). An improved combustion method of determining sulphur in iron and steel is described. The sample is burnt in oxygen and the SO_2 and SO_3 are absorbed in hydrogen peroxide to which methyl red is added; the resultant solution is titrated with NaOH. The difficulty in determining the end-point is overcome by the application of a potentiometric finish.

The Determination of Phosphorus in Steel Containing Titanium and Arsenic. A. T. Etheridge and D. G. Higgs. (Armaments Research Department, Woolwich : Analyst, 1946, vol. 71, July, pp. 316-317). In an earlier paper (*see* Journ. I. and S.I., 1941, No. I., p. 78 A) a method of determining phosphorus in steels containing up to 1% of titanium was described. In new tests a stronger titanium solution was used to avoid prolonged evaporation in the preparation of the synthetic steel solutions, and it has now been found possible to hold in solution titanium equivalent to 3% on sample; this quantity shows no sign of precipitation in the process originally described.

A Micro Filter Stick for Use in Spectrographic Analysis. G. E. Wilson. (Analyst, 1946, vol. 71, Aug., pp. 375-376). It is difficult to avoid mechanical loss when transferring microchemical quantities of solids from the filter to the cathode crater for spectrographic analysis. This danger may be eliminated and the analysis speeded up by converting the cathode carbon into a filter stick. A method of making such a filter stick is described.

BOOK NOTICES

(Continued from p. 83 A)

AMERICAN STEEL AND WIRE CO. "*Manual of Aircraft Materials. Cold-Rolled Strip, Wire and Wire Products.*" 4to., pp. 261. Illustrated. New Jersey, 1945 : American Steel and Wire Co.; London : United States Steel Export Co.

This manual has been prepared in an endeavour to supply a catalogue of aircraft materials and parts for ready reference, and to provide an intelligent approach to the problems

involved in the use of the Company's products. It traces the evolution of aircraft, and deals fully with control cables, cold-rolled steel strip, U-S-S stainless steel, wire, cold-finished steel bars, and springs. It also contains useful general engineering tables.

COCKRELL, W. D. "*Industrial Electronic Control. A Guide to the Understanding of Electronic Control Circuits for Industrial Uses.*" 8vo, pp. xii + 247.

Illustrated. New York and London, 1944: McGraw-Hill Book Co., Inc. (Price 14s.).

This book deals with electronic control circuits for industrial uses. The various sections deal with electron tubes, circuit components, basic electronic circuits, and industrial electronic circuits.

FERN, G. H. "*Training for Supervision in Industry.*" First ed. 8vo, pp. ix + 188. New York and London, 1945: McGraw-Hill Book Co., Inc. (Price 11s. 6d.).

This book explains the conference method of breaking down job problems and analysing them through group discussion and recommends it for accomplishing training. It deals specifically with such supervisory problems as maintaining mental health in industry, handling problems of women workers, promoting safety, training new workers, disciplinary problems, &c.

GUILLET, L. "*Les Métaux Légers.*" Tome II., Deuxième Partie, 8vo, pp. vi + 441-891. Illustrated. Paris, 1940: Dunod. (Price 30s.).

The present volume covers the utilization of aluminium and aluminium alloys; the properties, treatment and utilization of heavy alloys containing aluminium (including aluminium steel and aluminium cast-iron); magnesium and its alloys; beryllium and its alloys; and the alkaline metals, alkaline earths and their alloys.

LEWIS, WINIFRED. "*Thin Films and Surfaces.*" First ed. 8vo, pp. vi + 70. Illustrated. London, 1946: Temple Press, Ltd. (Price 15s.).

The first part of this monograph outlines present-day knowledge of the structure and properties of thin films and surfaces in general. The production of these films is also dealt with. The properties of aluminium are discussed in some detail and comparative data are given for other metals.

LIDDELL, D. M. "*Handbook of Nonferrous Metallurgy. Recovery of the Metals.*" Second ed. 8vo, pp. xi + 721. New York and London, 1945: McGraw-Hill Book Co., Inc. (Price 35s.).

This is the second part of a two-volume handbook; it deals with the metallurgy of each metal in detail. Facts are presented on the sources, production, uses and markets, the chemical, physical and mechanical properties, melting and casting, mechanical treatment, metallography, &c.

MACHU, W. "*Metallische Überzüge.*" 2 Auflage. 8vo, pp. xxiv + 643. Illustrated. Leipzig, 1943: Akademische Verlagsgesellschaft Becker und Erler Kom. Ges. (Lithoprint Copy, Ann Arbor, Michigan, 1945). (Price £6 10s.).

Part I. deals with the general and theoretical principles of corrosion and corrosion prevention, and metal-coating processes. Part II. deals with the production of metal coatings, their properties and testing.

RICKARD, T. A. "*The Romance of Mining.*" 8vo, pp. viii + 450. Illustrated. Toronto, 1945: The Macmillan Company of Canada, Ltd. (Price 19s.).

In this book, the author, who is a well-known authority on metal mining, has written a fascinating story of the discovery of all the famous mining properties, including the silver of Laurium, Frobisher's Quest, El Dorado, California gold, the Australian diggings, the gold of the North, and the diamonds of Kimberley and the Witwatersrand. The careers of notable men engaged in the development of these properties are sketched.

SAINT-MLEUX, J. "*Préparation des Surfaces Métalliques avant Peinture.*" Préface de M. Schueller.

Sm. 8vo, pp. 215. Illustrated. Paris, 1942: Dunod. (Price 7s. 6d.).

A study of modern industrial processes, covering degreasing, cleaning, and undercoating of ferrous and non-ferrous metal surfaces before painting.

SIMONS, E. N. "*Steel Castings.*" 8vo, pp. viii + 208. Illustrated. London, 1946: Paul Elek Publishers, Ltd. (Price 13s.).

This publication discusses in a general way the raw materials used and the methods for melting, pattern-making, and casting. The heat-treatment, machining, inspection and testing of steel castings are dealt with and the types of steel used are discussed. A number of typical steel castings are described and illustrated.

UNITED STEEL COMPANIES, LTD. "*Standard Methods of Analysis of Iron, Steel, and Ferro-Alloys.*" As used by the Laboratories of The United Steel Companies, Ltd. Third ed. 8vo, pp. 93. Sheffield, 1945: The United Steel Companies, Ltd. (Price 7s. 6d.).

This is the third edition of a deservedly popular work, the revision of which has brought it up to date and further enhanced its value to the metallurgical chemist interested in ferrous materials, although the methods described apply rather to the lower than the more highly alloyed steels. The first edition of this book was published in 1933, and the fact that essentially the methods are still very similar makes it clear that these have been well tried and proved to give accurate and reproducible results.

The scope and diversity of the various determinations show considerable amplification since the previous edition, so that the work has now developed into a reasonably comprehensive and standard book of reference for the ferrous analyst. The individual methods are well described in sufficient detail to avoid the pitfalls which the unwary or less experienced chemist has frequently encountered in the past. For example, the interferences from other chemical elements or fortuitous sets of conditions have been foreseen, and these appear to have been covered in a reasonably exhaustive manner by the notes at the end of each method described, references to which are given at the appropriate points in the text. Some criticism can be levelled at certain of the alternative methods but, generally speaking, they appear to be very sound.

Most of the more recent developments in metallurgical analysis have been incorporated in this new edition, of which the following are a few typical examples:

(a) In the gravimetric combustion method for the determination of carbon, the use of neutral precipitated manganese-dioxide for the absorption of sulphur gases not only makes the train liquid free, but also replaces four items in the trains, thus rendering it much shorter and more compact.

(b) In alloys of high chromium content, the removal of chromium as chromyl chloride allows the determination of aluminium by final precipitation with 8-hydroxyquinoline, a method which gives accurate and consistent results.

(c) The estimation of copper by the normal thiosulphate titration, interference from iron contamination being suppressed by the addition of sodium fluoride and urea.

Routine methods for the determination of the rarer elements such as columbium, zirconium, and selenium are given, and these will be found to be of particular value in view of the importance of these elements in modern steel metallurgy. It seems a pity that no method is included for tantalum, which invariably occurs with columbium; the one determination is complementary to the other.

The section dealing with ferro-alloys has been brought up to date by several alterations in methods, but in general this section shows little change as compared with the rest of the book.

It is pleasing to note the emphasis given in the Preface

to the need for using pure reagents; there is no doubt that in these days of extremely complex steels, when the need for high accuracy is even greater, this point cannot be impressed too strongly.

This book should be on the shelf of every laboratory dealing with the analysis of iron and steel.

E. GREGORY.

WALLACE, W. "*Enterprise First.*" 8vo, pp. 112. London, 1946: Longmans, Green and Co. (Price 8s. 6d.).

In this book the author seeks to reconcile the purposes of the State with the fullest practicable freedom for initiative

and enterprise in industry. He suggests how this can best be achieved in industries which are to be nationalized, but deals more particularly with the relation between the State and private enterprise.

WEEKS, MARY ELVIRA. "*Discovery of the Elements.*" Fifth ed., enlarged and revised. 8vo, pp. xiv + 578. Illustrated. Easton, Pennsylvania, 1945: Journal of Chemical Education.

The author traces the steps that led to the discovery of the various chemical elements and includes particulars of the careers of the discoverers and those who also played a part in revealing the hidden elements.

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TIRANTI, D., and W. F. WALKER. "*Introduction to Production Control.*" London: Chapman and Hall, Ltd. (Price 15s.).

MINERAL RESOURCES

(Continued from p. 17 A)

The Coal Resources of Scotland. M. Macgregor and W. J. Skilling. (Department of Scientific and Industrial Research: Institute of Fuel Bulletin, 1946, June, pp. 204-209). This paper deals in a general way with the distribution, classification, and available reserves of the coals of Scotland.

The Countries of South-Eastern Europe—Seen from the Metallurgical Point of View. I. Rumania. H. Loerzweiler. (Metallwirtschaft, 1940, vol. 19, June 14, pp. 497-501; June 21, pp. 517-529). A comprehensive review of the mineral resources, production of ores, their refining, and the manufacture of finished products in Rumania is presented.

Chromite-Bearing Sands of the Southern Part of the Coast of Oregon. A. B. Griggs. (United States Geological Survey, 1945, Bulletin No. 945-E). An account is given of the geology, location, and mining of the chromiferous sands, commonly known as "black sands," which are found in the southern part of the coast of Oregon.

Tungsten Deposits of the Southern Part of Sonora,

Mexico. J. M. Wiese and S. Cárdenas. (United States Geological Survey, 1945, Bulletin No. 946-D). Tungsten deposits occur in more than 20 localities in the southern part of the State of Sonora, Mexico. Production of tungsten was first recorded in 1916; since then a total of 100,000 short-ton units (one unit = 20 lb. of WO_3) has probably been produced in this region.

Exploration of the Piedmont Manganese Belt, McCormick County, South Carolina, and Wilkes County, Georgia. W. A. Beck. (United States Bureau of Mines, 1946, Apr., Report of Investigations No. 3858).

The Murzhik Deposit of Manganese Ores. P. P. Mikhailov. (Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS, 1945, vol. 48, No. 1, pp. 50-52). This paper contains the results of revisions and a reconnaissance of the Murzhik deposit of manganese ore, carried out in 1943. This deposit is 270 km. from Zhana-Semey station on the Turkestan-Siberian railway.

REFRACTORY MATERIALS

(Continued from p. 67 A)

The Silica Brick and Its Inventor, William Weston Young. R. Jenkins. (Transactions of the Newcomen Society, 1941-1942, vol. 22, pp. 139-147). A brief account is given of the early history of the development of refractory linings for metallurgical furnaces, together with a sketch of the life of William Weston Young (1776-1847). Various attempts had been made to bind silica sand without success until about 1820 when Young took up the matter and used lime as a binder. Young's method of making Dinas silica bricks is described.

Some Problems in the Manufacture of Refractories. R. E. Birch. (Ceramic Age: Refractories Journal, 1946, vol. 22, July, pp. 220-223). Methods by which problems in the manufacture of refractories have been overcome are reviewed. These include: (1) The Vignos method of drying ramming mixes by an exothermic reaction; (2) means of controlling the pressure applied in forming bricks; and (3) the determination of firing rates.

Physical Properties of Some High-Temperature Refractory Compositions. G. R. Pole, A. W. Beinlich, jun., and N. Gilbert. (Journal of the American Ceramic Society, 1946, vol. 29, Aug., pp. 208-222). Attempts to develop a refractory for use at 1800-2200° C. are described. Magnesia shapes, bonded with magnesium oxy-chloride and fired at 1450° C., gave satisfactory service in a furnace at 2000-2200° C. under oxidizing conditions. Additions of the relatively expensive oxides of beryllium, titanium, and zirconium lowered the coefficient of expansion of magnesia only slightly. This coefficient could be lowered considerably by additions of up to 50% of

chromic oxide, but as this oxide volatilizes when the temperature reaches about 2000° C., this mixture was not satisfactory.

The Behaviour of Refractory Materials under Stress at High Temperatures. Parts III. and IV. F. H. Clews, H. M. Richardson, and A. T. Green. (Transactions of the British Ceramic Society, 1946, vol. 45, May, pp. 161-176). In continuation of the work on the behaviour under compression of an insulating firebrick at 1200° C. described in Part II. (see Journ. I. and S.I., 1945, No. I., p. 92 A) further experiments have been conducted on much denser fireclay specimens at temperatures up to 1400° C. In each experiment the rate of deformation is rapid at first, but the rate decreases with time, tending to become linear at the higher temperatures and pressures of testing. In Part IV. the effect of the time of load application on the recovery of porcelain and fireclay from torsional strain at 1000° and 1100° C. is dealt with.

Third Report on Refractory Materials. (Iron and Steel Institute, 1946, Special Report No. 32). This Report, by the Joint Refractories Research Committee of the British Iron and Steel Research Association and the British Refractories Research Association, covers the period during which the whole pattern of research in the iron and steel industry has been organised. It is in six Sections. Section A, which is introductory in character, consists of a Foreword by R. A. Hacking and A. T. Green explaining the nature of the Report, as well as lists of members of the Committees and Panels concerned with different spheres of the research work. Since the Basic Bricks

Sub-Committee was set up in 1941, increasing stress has been laid on the study of chrome ore, and the spinels and complex solid solutions formed in chrome-magnesite refractories. This work is dealt with in Section B. Section C comprises papers on basic open-hearth refractories and their reactions with slags. Sections D and E deal respectively with casting-pit and electric-steel-furnace refractories, whilst Section F, which concludes the Report, contains a summary of other published work of the British Refractories Research Association which is of interest to the iron and steel industry. Abstracts of the papers follow.

The Genesis of Chrome Ores. A. E. Dodd and A. T. Green. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 7-30). The hypotheses which have been put forward to account for the formation of chrome ore bodies are briefly reviewed. It is now considered that the ore may be either magmatic or hydrothermal in origin. The geological literature on the world sources of chrome ore is examined, and the mineral associations and probable mode of genesis of each deposit are described. The bibliography contains 105 references.

The Constitution of Chrome Ores. Part I. The Composition and Properties of the Chromite Grains in Certain Chrome Ores. W. Hugill and A. T. Green. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 31-41). Seventeen samples of chrome ores from nine localities have been analysed. The composition, refractive index, and specific gravity of the separated chrome grains have been determined and the proportions of chrome grains and gangue in each sample calculated. A preliminary investigation of differing behaviour of the samples under chemical attack has also been made.

An Investigation of Chrome Ores. Part I. The Action of Reducing Gases on a Number of Chrome Ores. G. R. Rigby, G. H. B. Lovell, and A. T. Green. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 43-80). The investigation is concerned with the increase in size and tendency to friability which certain chrome products exhibit when subjected to a reducing atmosphere. It has been found that raw ores were not affected by reducing conditions, but that certain fired ores increased in size with marked crumbliness. A method of estimating the FeO and Fe₂O₃ contents of chrome ores is described. It is shown by this method that on firing chrome ores, spinels containing FeO tend to be oxidized to solid solutions of sesquioxides (R₂O₃). On exposing these oxidized chrome ores to reducing gases the solid solution is again reduced to the spinel, but this reduction is accompanied by an increase in volume of the chrome grains. The tendency for fired chrome ores to grow in a reducing atmosphere is determined by (1) the texture of the specimen, particularly the permeability to gases; (2) the constitution of the chrome grains; and (3) the nature and amount of the gangue minerals. Reaction occurs between oxidized chrome grains and a serpentine gangue resulting in a tendency for Fe₂O₃ to pass out of the chrome grains with the simultaneous entry of MgO into the grains. The absorbed MgO restores the spinel balance of the chrome grains, the

iron oxide being present as MgO.Fe₂O₃. This reaction helps to stabilize the product to reducing gases.

An Investigation of Chrome Ores. Part II. The Effect of the Constitution of the Chrome Grains on the Action of Reducing Gases. G. R. Rigby, G. H. B. Lovell, and A. T. Green. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 81-92). A number of synthetic compositions containing the spinels MgO.Al₂O₃, MgO.Cr₂O₃, MgO.Fe₂O₃, and the solid solutions Fe₂O₃.2Al₂O₃ and Fe₂O₃.2Cr₂O₃ have been prepared. The compositions were exposed to the action of hydrogen over the temperature range 650-1050° C. The rates of reduction were determined by measuring decreases in weight. The increases in length undergone by these compositions were also studied. It was found that the increases in length did not run parallel to the amounts of reduction. For a constant iron oxide content, volume increase was favoured by a high Cr₂O₃ content and reduction by a high Al₂O₃ content. The results obtained for fired chrome ores have been reviewed in the light of the deductions drawn from the behaviour of the various synthetic compositions.

An Investigation of Chrome Ores. Part III. The Properties of the Spinel Chromite and Hercynite. G. R. Rigby, G. H. B. Lovell, and A. T. Green. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 93-100). The spinels chromite FeO.Cr₂O₃ and hercynite FeO.Al₂O₃ have been prepared and some of their properties determined. Data for the reversible thermal expansions and densities of both the spinels and their oxidation products Fe₂O₃.2Cr₂O₃ and Fe₂O₃.2Al₂O₃ are given. The action of hydrogen and oxygen on chromite, hercynite and their corresponding oxidation products are also reported.

An Investigation of Chrome Ores. Part IV. The Action of Iron Oxides on Spinel and Chrome Products. G. H. B. Lovell, G. R. Rigby, and A. T. Green. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 101-151). The action of iron oxides on synthetic spinels, magnesia, and specimens made from selected chrome ores has been studied, primarily with a view to investigating the bursting expansion which occurs in service when refractory materials containing chrome ore are exposed to iron oxide slags. The following tests have been carried out: (1) Firing mixes of spinels and related products with ferric oxide additions at various temperatures up to 1600° C. in air; (2) heating metallic iron on the top face of cubes of various materials at 1400° C. in air; (3) melting ferrous oxide on specimens at 1400° C. in nitrogen; (4) melting magnetite on specimens at 1600° C. in nitrogen; (5) melting suitable mixtures of ferrous oxide and magnetite on specimens at 1400° C.; (6) heating intimate mixtures of magnetite and various materials moulded into cylinders at 1400° C. in nitrogen; and (7) subjecting specimens composed of various materials and ferric oxide previously heated either at 1200° C. or 1500° C. to hydrogen at temperatures ranging from 450° to 1050° C.

Unless magnetite was present due to oxidation, ferrous oxide did not give bursting expansions with magnesia nor spinels, but only with chromic oxide

and alumina. Pure magnetite and iron oxide mixtures containing magnetite gave bursting expansions with spinels, chromic oxide, and alumina, but not with magnesia. The mechanism by which magnetite produces expansions when in contact with various materials has been discussed at some length and appears to have its origin in forces set up due to crystallization occurring in specific directions. The relationship between the magnitude of the bursting expansion with chrome ores and the physical and chemical characteristics of the ores is discussed in some detail. The constitution of the chrome grains, the amount and nature of the gangue minerals, the extent of reaction between gangue and chrome grains, the size of the chrome grains and the porosity, permeability, and mechanical strength of the material are among the factors influencing the bursting expansions of chrome products.

An Investigation of Chrome Ores. Part V. Volume Changes Occurring when Binary Mixtures of Spinel Are Heated between 800° and 1400° C. G. H. B. Lovell, G. R. Rigby, and A. T. Green. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 153-174). The bursting expansion which has previously been shown to take place when magnetite is melted on chrome ores and certain spinels has been further investigated. Bursting expansions have been determined on binary mixtures of numerous spinels by heating the intimate mixtures at various temperatures between 800° and 1400° C. and measuring any increases in diameter of the specimens.

It has been shown that, in general, the chromite spinels and, to a lesser extent, the aluminate spinels give bursting expansions with ferrites and sometimes with those titanates and stannates which possess a spinel-type lattice. On the other hand, chromites show no bursting phenomena with aluminate spinels, while ferrites, titanates, and stannates do not give bursting expansions when mixed together among themselves.

A theory has been advanced suggesting that the bursting expansion is caused by a rearrangement of the metal atoms in the space lattice which occurs during solid solution. Some X-ray data have been quoted which tend to support this hypothesis.

An X-Ray Investigation into the Constitution of Chrome Ores. J. R. Rait. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 175-209). X-ray powder photographs have been taken of chrome ores, both in the raw state and after firing under oxidizing and reducing conditions. Similar photographs have been obtained of the spinels $\text{MgO} \cdot \text{Al}_2\text{O}_3$, $\text{MgO} \cdot \text{Cr}_2\text{O}_3$, $\text{MgO} \cdot \text{Fe}_2\text{O}_3$, $\text{FeO} \cdot \text{Al}_2\text{O}_3$, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, and of a range of their solid solutions with each other. The solid solutions of $\text{Al}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$ and Fe_2O_3 have likewise been examined.

It is concluded from the X-ray and analytical data that chrome grains in chrome ores consist mainly of balanced spinels ($\text{RO} \cdot \text{R}_2\text{O}_3$), but in two chrome ores the spinel was unbalanced, excess alumina being dissolved as $\gamma\text{Al}_2\text{O}_3$. On firing in an oxidizing atmosphere the spinel oxidized to form two phases consisting of a magnesium spinel and a solid solution of $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ and Cr_2O_3 . The amount of R_2O_3

formed appears to be proportional to the FeO/MgO ratio. Certain ores did not readily oxidize, this being ascribed to their high Al_2O_3 content. On subsequent reduction in hydrogen, R_2O_3 disappeared and the ores containing a high content of R_2O_3 became friable. When chrome ores containing a magnesian gangue were fired, interaction with the R_2O_3 to form $\text{MgO} \cdot \text{R}_2\text{O}_3$ occurred, decreasing the susceptibility to reduction in hydrogen. The ferromagnetic properties of the ternary system MgFe_2O_4 - MgCr_2O_4 - MgAl_2O_4 have been examined and the results provide evidence supporting the oxidation theory.

The chrome ores have been classified in order of susceptibility to friability during firing. A commercial chrome-magnesite brick fired in a reducing atmosphere at 900° C. showed no growth, but it disintegrated.

The Effect of Precalcination on Friable Chrome Ores. N. E. Dobbins and W. J. Rees. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 211-233). Various size-gradings of a Transvaal chrome ore which develops friability on firing have been calcined for 2 hours at 1550° C. with different proportions of (a) serpentine, (b) serpentine and magnesite, (c) dolomite, (d) stabilized dolomite, and (e) lime, in a laboratory gas-fired furnace. The sieve analyses of the crushed products, the expansion or contraction on refiring the clinker with finely ground magnesite, and the iron oxide bursting expansion of the resultant products have been determined. Clinker was also prepared in a works rotary kiln from 18 cwt. of the chrome ore and 2 cwt. of finely ground serpentine and similarly examined. The results have been considered in conjunction with information on the nature of the reactions taking place obtained from X-ray analysis and microscopic examination of the products.

The laboratory trials using serpentine demonstrated the beneficial action of the calcination with serpentine and indicated that the best results were obtained if the original ore was finely ground. The works trial only partially confirmed the results obtained in the laboratory. The calcination with dolomite, stabilized dolomite, or lime, resulted in an increase in the yield of grains suitable for brick manufacture, but the change in the iron-oxide bursting expansion was indefinite. The chrome-ore/lime clinkers were the most promising in this respect.

Some Investigations on the Draining of Slags at High Temperature. N. E. Dobbins and W. J. Rees. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 235-255). A basic open-hearth slag on heating very quickly to 1350° C. was found to be completely fluid, whereas on heating slowly no signs of fusion appeared even at 1650° C. Visual observations indicated that something had drained from the slag on heating slowly, leaving a skeleton of greater refractoriness than the original slag. This was confirmed by heating slag pills of known weight to various temperatures, cooling, and noting the loss in weight; the extent of draining was found to depend mainly on the firing temperature. A basic electric oxidizing slag, an acid open-hearth slag, and synthetic slags were found to behave similarly.

Analyses of the basic open-hearth slag after heating to different temperatures showed that marked changes in composition had occurred. Calculations based on the amount of draining and the analyses of the residual slags indicate that at 1450° C. compounds of the approximate composition $2\text{CaO} \cdot \text{R}_2\text{O}_3$ drain away, while between 1550° C. and 1650° C. the drainage liquid consists mainly of calcium phosphates, silicates, and/or silicophosphates. After firing to 1650° C. the analysis of the residual slag approximates to a mixture of calcium orthosilicate and calcium phosphates.

With progressive draining, the fusion point of the residual slag increases. As draining also takes place in slag-refractory mixtures, marked discrepancies may result in fusion curves determined by the customary cone method. The discrepancies liable to be encountered whilst conducting "pill-type" slag tests are discussed, and evidence confirming these possible errors is presented. Methods for overcoming these discrepancies are suggested, and tests have been conducted on these lines.

The amount of draining from slag-refractory mixes at widely different rates of heating and the rapidity of draining of some of the mixes have been investigated. In all the cases studied the draining appeared to be complete after 10 minutes at a constant temperature. Although the amount of draining depends mainly on the amount of slag in the mix and the firing temperature, other factors, such as the amount of low-melting-point constituents contained by the refractory, also affect the results.

The industrial significance of the draining of slags is indicated, and the possible heterogeneity of refractory materials caused by a similar process has been pointed out; evidence of the latter has been given.

The Behaviour of Basic Bricks in the Open-Hearth Furnace. G. R. Rigby, G. H. B. Lovell, and A. T. Green. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 257-273). A description is given of the petrological features of basic bricks which have been in service in the back walls of basic open-hearth furnaces. The bricks include chrome-magnesite, chrome-magnesite-olivine, and magnesite-olivine products. From the data obtained the various chemical reactions undergone by the chrome, magnesia, and olivine are discussed. Chrome absorbs iron oxide and also reacts with a forsterite matrix, giving magnesioferrite and pyroxenes. Magnesite is converted into magnesioferrite and at the working face of the bricks no free magnesia is present. The olivine tends to lose magnesia with conversion into pyroxenes or glass. It is suggested that in basic bricks of the chrome-magnesite-olivine type, the chrome, magnesia, and silica contents should be carefully controlled to give optimum life in the furnace.

The Fusion Relations of the Ternary System Magnesite/Calcined-Dolomite/Basic-Slag and of Other Basic Refractory Materials with Basic Open-Hearth Slag. N. E. Dobbins and W. J. Rees. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 275-286). The fusion relations of the ternary system magnesite/dolomite/basic-slag have been determined. At temperatures up to 1650° C. all mixtures of magnesite and dolomite behaved similarly. The maximum

amount of free lime permissible in basic refractories without exerting detrimental effects during its storage has been shown to be very low.

Although a mixture possessing the eutectic composition between lime and magnesia (to which composition dolomite approaches) has similar fusion relations with basic slag to dolomite, lime itself has a much greater solubility in the slag than any of the other mixtures examined. The fusion relations of lime and magnesia with basic slag have been shown to be similar to their relations with ferric oxide. The behaviour of the eutectic composition could not be explained satisfactorily, but a parallel case has been cited in the system $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3$.

The fusion relations of both $3\text{CaO} \cdot \text{SiO}_2$ and $2\text{CaO} \cdot \text{SiO}_2$ with basic slag have been investigated. Up to 1650° C. the former was found to be comparable with that of magnesite, whilst the latter behaved similarly to a stabilized dolomite product in which the lime was present essentially as $3\text{CaO} \cdot \text{SiO}_2$. The relations of CaO , $3\text{CaO} \cdot \text{SiO}_2$, and $2\text{CaO} \cdot \text{SiO}_2$ with basic slag have been compared, and the similarity to their behaviour in the presence of alumina indicated. The possible use of $3\text{CaO} \cdot \text{SiO}_2$ as a refractory has been suggested. The major difficulties likely to be met in its use have been pointed out and their importance discussed.

The solubilities of magnesite, dolomite, $3\text{CaO} \cdot \text{SiO}_2$, stabilized dolomite, and $2\text{CaO} \cdot \text{SiO}_2$ in "silica wash" have been considered theoretically and found to be in the above order. The mutual fluxing effect of magnesia and calcium silicates in the presence of basic slag has been indicated.

An Examination of Magnesite Bricks Attacked by Iron Oxide Slags. G. R. Rigby and A. T. Green. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 287-291). A petrological examination of magnesite blocks taken from the lining of an inactive metal mixer has been described. The types of reactions which were found to occur at the hot face of these blocks appear to be similar to reactions which take place in magnesite-olivine bricks when used in the back-walls of open-hearth furnaces. These reactions were described by the authors in an earlier paper.

Observations on Ladle Linings Used in the Casting of Basic Open-Hearth Steel. A. E. Dodd and A. T. Green. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 293-322). Observational work has been carried out on ladle linings at three steel-works. The variations in the factors affecting ladle life have been studied and have been correlated with the wear of the ladle lining; the total wear was determined by actual measurement of the used bricks, and the wear for each cast was calculated from the change in slag composition during teeming. Four brands of brick were used, thirteen linings (120 casts) being followed from bricking to the final knocking out.

Of the factors which determine the life of the lining, it is concluded that the weight of the slag carried on the ladle is the most significant; abrasion by the stream of metal from the furnace during tapping is also important. The rate of solution of the refractory by the slag appears to be controlled by the slag

basicity; the reaction proceeds in the direction of anorthite formation. Fluid ferruginous slags penetrate the pore system of the ladle lining more deeply than the viscous limy slags; however, this penetration does not appear to be accompanied by much actual solution of the brickwork.

From the work carried out it would seem that aluminous ladle bricks (38% Al_2O_3) are no more durable than dense well-fired siliceous bricks (30% Al_2O_3). It has been confirmed that under-burned ladle bricks have a shorter life than well-fired products made from the same clay.

Report of the Casting-Pit Refractories Sub-Committee of the Open-Hearth Refractories Joint Panel. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 323-347). The work done by the Casting-Pit Refractories Sub-Committee since its first meeting in 1941 is reviewed. A large proportion of this work has been devoted to the simplification of the sizes and shapes of casting-pit refractories; standard sizes for stoppers and sleeves are recommended and are meeting with the approval of an increasing number of steel plants and foundries. Valuable data on the durability of runner bricks and the entrapment by the steel of inclusions derived from this source are presented and discussed.

Report of the Electric Furnace Refractories Sub-Committee. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 349-379). A survey is made of the design and life of the roofs of seventeen electric-arc steel furnaces; relevant features of operation are also tabulated. On the basis of the data collected it is concluded that the longest life is normally obtained from roofs of the domed, fixed, type; flat-centred movable roofs are reported to have given, in general, a shorter life, with spalling the chief cause of failure. Amongst other factors which influence the roof life are the nature of the refractories used, the expansion allowance and rise of the arch, the rate of initial warming up, and the power input as it affects the temperature attained during melting and refining. Certain of these factors have been examined in detail; for example, power-input schedules have been compared at different works, temperature records have been kept during the heating up and operation of an arc furnace, and the effectiveness

of different kinds of expansion-joint filling have been compared. Used roof bricks have been examined by microscopical and X-ray methods. An important result of this phase of the work is the observation that tridymite appears to be the stable phase of silica at the working face of an arc-furnace roof; this would indicate that the actual surface of the roof is normally at a temperature below 1470°C ., the upper limit of stability of the tridymite form of silica.

On the basis of the information collected, and of the joint experience of the Committee, a simplified, domed, roof design has been developed. A considerable number of roofs have now been built to this recommended design and have given satisfactory lives. The main features of the recommended roof are the use of small correctly shaped bricks, built to a standard rise, with expansion joints at stipulated intervals. Roofs are divided into three classes: Group A, 12-15 ft. diameter; Group B, 8-12 ft. diameter; Group C, 5-8 ft. diameter. A roof of any group can be accurately constructed using six sizes of arch brick, one size of skewback brick, one special centre brick, and one size of side-arch brick for the electrode rings. Full details are given for the construction of roofs to this recommended pattern.

In the final section of the report the results of service trials at three steelworks with this type of roof are given in some detail.

Summary of Other Work of the British Refractories Research Association of Interest to the Iron and Steel Industry. (Iron and Steel Institute, 1946, Special Report No. 32, pp. 381-387). Research work carried out by the British Refractories Research Association on basic refractories, silica refractories, the action of slags and gases on refractory materials, the behaviour of refractory materials under stress at high temperature, the manufacture of insulating bricks, and the desirable properties of monolithic cements, is reviewed.

New Mineral Wool Insulation Standard. (Steel, 1946, vol. 119, Sept. 2, pp. 120-122). It is announced that the National Bureau of Standards and the Industrial Mineral Wool Institute have issued Standard CS-131-46 on methods of testing all forms of mineral wool insulation.

FUEL

(Continued from pp. 85 A-86 A)

Gas Turbines. (British Engineering Export Journal, 1946, vol. 29, Sept., pp. 331-333). An illustrated description is given of an experimental gas-turbine plant designed by C. A. Parsons & Co., Ltd., designed for an output of 500 h.p. at 6000 r.p.m.

The Dewatering of Washed Small Coal. F. Hopkinson. (Year Book of the Coke Oven Managers' Association, 1946, pp. 145-159). Methods of reducing the free water content of washed small coal are critically examined.

The Ideal Coking Plant. T. W. Mills. (Year Book of the Coke Oven Managers' Association, 1946, pp.

230-241). On the basis of experience with existing coke-oven and by-product plants the author discusses factors affecting plant layout and design, and describes an ideal plant.

Planning for Electrical Maintenance and Extensions. W. Fordham Cooper. (Year Book of the Coke Oven Managers' Association, 1946, pp. 215-227). The organization of electrical work in connection with extensions and reconstruction of coke-oven plants is described and discussed.

The Flow of Gases in Coke Oven Systems. D. T. Barritt and R. J. Barritt. (Year Book of the Coke

Oven Managers' Association, 1946, pp. 274-291). The principles influencing the flow of gases in coke-oven systems were dealt with by the authors in an earlier paper (see Journ. I. and S.I., 1946, No. I., p. 2 A). In the present paper these principles are dealt with in more detail, and it is shown how they can be applied to the assessment of good and bad features in coke-oven heating systems.

Drying, Briquetting, and Low-Temperature Carbonisation of Brown Coal in Lurgi-Spülgas Retorts. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 626: H.M. Stationery Office).

Inspection of Krupp-Lurgi Plants for the Carbonisation of Coal at Low Temperatures. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 616: H.M. Stationery Office).

The Design, Operation, and Control of Distillation Plant, with Special Reference to Refining of Benzole. J. Hamilton. (Year Book of the Coke Oven Managers' Association, 1946, pp. 199-211).

The Continuous Tar Distillation Still at Gesellschaft für Teerverwertung. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 615: H.M. Stationery Office). A description is given of the continuous vacuum still for the fractionation of dehydrated high-temperature tar at the Duisberg-Meiderich Works of the Gesellschaft für Teerverwertung.

Developments in Gas-Producer Construction and Performance. A. G. Arend. (British Steelmaker, 1946, vol. 12, Aug., pp. 406-409). The developments in gas producers which are discussed include: (1) A carbonizing shaft in which lignite briquettes are heated, dried, and precarbonized before passing into the producer shaft proper; (2) special stirring and charging devices; (3) cooling systems; and (4) smaller rotary-grate producers with a pre-cooler and gas washers which can be used with either low-temperature coke from lignite or anthracite without making structural alterations.

PRODUCTION OF IRON

(Continued from pp. 86 A-87 A)

Swedish Mining Developments in Recent Years. M. Wiberg. (Jernkontorets Annaler, 1946, vol. 130, No. 8, pp. 285-312). (In Swedish). During the war years 1939-1945 the Swedish mining and metal-producing industries worked under very great difficulties, caused mainly by the shortage of fuel and labour. The methods adopted by the producers of both ferrous and non-ferrous metals to meet these difficulties are reviewed in this paper which also gives some production statistics.

Opening a Chilled Blast-Furnace Hearth. R. P. Towndrow. (Iron and Coal Trades Review, 1946, vol. 153, Aug. 30, pp. 349-352). The condition in a blast-furnace when it is impossible to tap either metal or slag in the normal manner, is discussed and suggestions are put forward for dealing with the situation.

German Methods of Manufacture of Copper Tuyeres for Blast Furnaces. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 670: H.M. Stationery Office). An account is given of the methods employed at five German works manufacturing copper tuyeres for blast-furnaces.

A New Automatic Casting Machine for Producing Ingots and Pigs. K. Hoffmann. (Zeitschrift für Metallkunde, 1944, vol. 36, Feb., pp. 46-48). A description is given of a pig-casting machine in which the chills are mounted on a turntable driven by a motor. The feeding ladle is part of the machine, and the tilting of the ladle is automatically controlled by triggers underneath the chills operating the tilting mechanism in such a way that the spout is lowered only when a chill is in position below it.

Sintered Iron and Steel Components. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 595: H.M. Stationery Office). This is a

report on visits to five German works manufacturing driving bands for shells, small bearings, and other iron and steel parts by powder metallurgy.

Properties of Sintered Iron-Copper Powders. F. C. Kelley. (Iron Age, 1946, vol. 158, Aug. 15, pp. 57-60). A study was made of the effects of variation in sintering temperature, sintering time, and copper content of copper-iron bars containing up to 30% of copper, made by the powder-metallurgy process. The strength and ductility of 5/95 copper-iron bars when pressed and sintered for 30 min. at from 2010° to 2460° F. increased with the temperature. With 10/90 copper-iron bars sintered at 2010° F., the strength and ductility increased with the sintering time. Tests on mixtures ranging from 5% to 30% of copper indicated that there is little to be gained in strength by increasing the proportion of copper.

Powdered Metal vs. Other High Production Methods. H. Chase. (Materials and Methods, 1946, vol. 24, Aug., pp. 363-369). Some of the factors which demand consideration in determining whether particular parts should be made by powder metallurgy or by other methods are pointed out. The size, weight, and shape limitations, rates of production, tooling costs, and dimensional accuracy of powder-metallurgy products are discussed.

The Statistical Approach in Industrial Research. A. Lesser, jun. (Iron Age, 1946, vol. 158, Aug. 22, pp. 50-55). An account is given of the statistical method which was applied to study the effects of changes in three factors affecting the strength of iron bars made by the powder-metallurgy process. The mathematical technique, which is fully explained, is equally applicable to other metallurgical problems.

FOUNDRY PRACTICE

(Continued from pp. 87 A-89 A)

Analysis of the Gray Iron Casting Industry. (Foundry, 1946, vol. 74, Aug., pp. 96, 214). Statistics on the capacity of iron foundries and the production of iron castings in the United States are presented in extracts from a report issued by the Bureau of the Census of the U.S. Department of Commerce.

The Production and Application in Germany of High Silicon and Acid Resisting Iron. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 594: H.M. Stationery Office). Details are given of investigations at several German foundries manufacturing high-silicon acid-resisting cast irons. A comparison is made between German and British experiences in the manufacture of this iron during the war years.

Theories of Gray Cast-Iron Inoculation. H. W. Lownie, jun. (American Foundrymen's Association, 1946, Preprint No. 46-39). The factors affecting the size and distribution of the graphite flakes in cast iron and three theories to explain the mechanism of inoculation are discussed. (See Journ. I. and S.I., 1945, No. II., p. 132 A).

Annealing Rate in Gaseous Malleablising. D. M. Dovey and I. Jenkins. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 80, Sept. 19, pp. 63-68). The new gaseous process of producing whiteheart malleable iron has already been described (see Journ. I. and S.I., 1945, No. II., p. 80 A). The conditions under which this process is carried out will probably permit the application of a formula relating the time of annealing, the mean residual carbon content of the annealed iron, and the thickness of the casting. In this paper curves for these relationships are developed and compared with curves from experimental data for an iron of the following composition: Carbon 3.24%, silicon 0.52%, manganese 0.16%, sulphur 0.24%, and phosphorus 0.07%.

The Influence of Raw Material on the Properties of Whiteheart Malleable Cast Iron with Special Reference to the Influence of Residual Elements. (Institute of British Foundrymen, 1946, Paper No. 849). This report was prepared by the Malleable (Metal Compositions) Sub-Committee appointed in 1942 by the Technical Advisory Panel to the Directors for Iron Castings, Ministry of Supply. It deals with investigations of the differences which have occurred in the properties of malleable castings produced from mixtures containing in some cases refined iron, and in others mixtures of hematite iron and steel scrap. The influence of residual elements and of using burnt ingot-mould scrap in the production of refined iron were also studied. Nickel in amounts up to 0.3% can be present in annealed whiteheart malleable cast iron without harm. Copper up to 0.7% had no adverse effects on larger sections, but tended to reduce the ductility of small sections ($\frac{3}{8}$ in.). Chromium up to 0.2% had no harmful effects under the conditions studied, neither had molybdenum in amounts up to 0.2%; these two

elements tended to reduce the expansion on annealing of the larger sections and to increase the contraction in the small sections. Tin and boron (in amounts greater than 0.1%) behave in a similar manner. Heavy relative decarburization, such as is experienced by $\frac{3}{8}$ -in. sections, tended to obliterate the effects of the residual elements except when they produced mottling in the original casting. No significant differences between refined iron and hematite-steel melts were recorded. No evidence was obtained that melting in contact with oxidized material caused the production of inferior malleable iron.

High-Tensile Alloy Steel Castings. J. F. B. Jackson. (Association of Mining Electrical and Mechanical Engineers, West of Scotland Iron and Steel Institute, and Institute of British Foundrymen, Joint Meeting: Foundry Trade Journal, 1946, vol. 80, Sept. 26, pp. 83-89). The melting of steel in the steel foundry, cement-sand moulding, centrifugal casting, and radiographic inspection are briefly described and some special war-time applications of high-tensile steel castings are discussed.

The German Steel Castings Industry. C. W. Briggs and M. T. Ganzauge. (United States Bureau of Mines, 1946, Information Circular No. 7362). The results of an investigation of the methods employed at large, medium, and small steel foundries in Germany are reported.

German Steel Foundries. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 716: H.M. Stationery Office). A report is presented on visits to 14 German steel foundries. Details are given of the castings produced, the steelmaking processes, and the moulding and casting practice.

The Fundamental Characteristics of Moulding Sands. W. Davies. (Iron and Steel Institute, 1946, this Journal, Section I.). Moulding sands may be prepared by mixing sand and clay (synthetic moulding sands) or they may be naturally occurring mixtures of sand and clay (naturally bonded moulding sands). Both synthetic and naturally bonded sands should be composed of two size-grades only, viz., the sand grade and the clay grade, that is, of particles 1.0-0.1 mm. in dia. and particles less than 0.01 mm. in dia. The proportion of grains of other sizes should be small. The behaviour of a moulding sand in foundry practice depends on its fundamental characteristics, such as: Plasticity, permeability, strength, and refractoriness; these characteristics are determined by the shape, mechanical grading, and mineralogical constitution of the two grades.

In this paper the geological characteristics are discussed, particularly as regards the mineralogy of the clays. The mechanism of the bonding of moulding sands is reviewed in the light of recent hypotheses; this is followed by a detailed discussion of the effects of different types of clay on the moulding properties of a sand as a whole.

Sand Reclamation for the Ferrous Foundry. E. C. Jeter. (American Foundrymen's Association:

Foundry, 1946, vol. 74, Aug., pp., 86-89, 172-178). The advantages and disadvantages of the wet and dry methods of sand reclamation are discussed.

Drying of Foundry Sand Cores by Dielectric Heat. J. R. Calhoun, L. E. Clark, and H. K. Salzberg. (Industrial Heating, 1946, vol. 13, July, pp. 1179-1189). The theory of dielectric heating is explained and its advantages for drying cores are pointed out, the principal one being the great saving in the drying time. The results of drying tests on cores weighing 4 oz., 6 lb., and 40 lb. are given.

Induction and Dielectric Heating. (Metallurgia, 1946, vol. 34, Aug., pp. 210-212). The principles involved in the application of induction and dielectric heating are compared. One of the advantages of dielectric heating is that equal amounts of heat are generated in every section of the mass of material. The method is therefore valuable for drying cores and moulds in the foundry and for the polymerization of thermosetting plastics. It has been found that, using thermosetting binders, cores can be baked at great speed, small ones requiring only 30 sec.

Producing Cast-Iron Rolls. P. Dwyer. (Foundry, 1946, vol. 74, Aug., pp. 92-93, 224-232). A description is given of the melting and casting technique developed at the iron foundry of the Bethlehem Steel Company for making chilled rolls.

Casting Turbogenerator Parts. (Foundry, 1946, vol. 74, Aug., pp. 90-91). A description is given of the moulding methods adopted for a turbo-generator casting weighing 65 tons.

A Comparison of Precision Casting Methods. W. A. Morey. (American Foundrymen's Association: Foundry, 1946, vol. 74, Aug., pp. 85, 216-220). The advantages and limitations of the lost-wax process, plaster-mould casting and centrifugal casting are reviewed and compared.

Fluidity Testing of Foundry Alloys. K. L. Clark. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 79, Aug. 29, pp. 443-450; vol. 80, Sept. 5, pp. 11-16). A comprehensive review of the literature on fluidity tests is presented, together with a bibliography containing 105 references. Recommendations for a standard fluidity test are made.

PRODUCTION OF STEEL

(Continued from pp. 89 A-94 A)

A Design of a Steel Plant Suitable for the Lincolnshire District. J. B. R. Brooke. (Presidential Address, Lincolnshire Iron and Steel Institute, 1946). An outline is given of the principal features of the design of a plant to produce about 550,000 tons of ordinary steels and about 200,000 tons of special steels per annum using the phosphoric ores of the Lincolnshire district. The mass-production shop would consist of one 2000-ton mixer and six 300-350-ton tilting furnaces, and the second shop of three 150-ton fixed one-way-fired recuperative furnaces.

Production Planning. J. F. Black. (Iron and Steel Engineer, 1946, vol. 23, Aug., pp. 60-62). The organization of a department for planning the production of a large steelworks is described.

Random Notes on Chinese Steel Industry. J. K. Stafford. (Metal Progress, 1946, vol. 50, Sept., pp. 470-473). Some experiences of an American engineer who visited Chungking in 1945 to assist the Chinese in the production of iron and steel are related. The blast-furnaces produce from 20 to 60 tons of iron per day. There are five open-hearth furnaces, the largest being a 15-ton furnace fired with producer gas. Many of the rolling-mills are driven by salvaged marine engines. These circumstances are due to the industry working in a completely blockaded area.

Soviet Steel. (Freyn Design, 1946, Sept., pp. 14-15). Data on the production of some of the large blast-furnaces and open-hearth furnaces in the U.S.S.R. are presented. The designs of these furnaces have been standardized on the basis of American experience.

Japan—The Rise and Fall of Industrial Development. (British Iron and Steel Federation, Monthly Statistical Bulletin, 1946, vol. 21, Aug., pp. 1-7).

A brief account is given of the expansion of the heavy industries of the Japanese empire up to 1943 and of their subsequent decline. The home islands and the "inner zone", comprising Manchuria, Korea, and occupied China, are dealt with separately.

Brazil Makes Steel. (Freyn Design, 1946, Sept., pp. 1-5). A description is given of the plant and layout at the integrated iron and steel works which has just commenced production at Volta Redonda in Brazil. There are two 150-ton fixed furnaces and one 150-ton tilting furnace with an annual production capacity of 270,000 metric tons.

The Melting Shop of the Turkish State Iron and Steel Works, Karabük. L. Cook. (Iron and Steel Institute, 1946, this Journal, Section I.). An account is given of the open-hearth plant and practice at the Karabük Iron and Steel Works, which commenced steelmaking operations in 1940. The plant is situated near the Zonguldak coal area, in Asia Minor, and was established by the late Kemal Atatürk as part of the scheme for the industrialization of modern Turkey. Turkish ores of low phosphorus and sulphur content, and other raw materials obtained within the country, are used in the plant for the production of the iron.

The melting shop contains four fixed furnaces of modern design, each of 65 tons capacity. The furnaces are fired with coke-oven and blast-furnace gas, which is pre-mixed at a central station and conveyed to the shop through a common main. The charges consist of scrap, and hot metal received direct from the blast-furnace. Ore additions are made in the runner and ladle to hot iron that is judged to have a silicon content higher than the desired limit. Details of the furnaces and the materials used are given, together with descriptions of the steel-making and casting practice for the production of

ingots designed for rolling in the mill, without a preliminary reduction in a cogging mill. Summaries of performance figures are included, with a mention of difficulties arising from wartime conditions of supply. Brief accounts of controls, and a description of methods used for training personnel, conclude the paper.

Pipemaker Starts Large Improvement Program. J. D. Knox. (Steel, 1946, vol. 119, Aug. 19, pp. 132-134, 150-152). A description is given of the new coke-ovens, Bessemer plant, soaking-pits, rolling-mill, and welding plant under construction for the National Tube Company, Lorain, Ohio.

Crucible Melting with Coke or Gas. (British Steelmaker, 1946, vol. 12, Sept., pp. 436-438). Descriptions are given of working conditions in the crucible melting of steel in coke- and gas-fired furnaces in the period 1900-1910.

Open-Hearth Operations at Wickwire-Spencer Steel. J. B. Fleming. (Iron and Steel Engineer, 1946, vol. 23, Aug., pp. 79-81). The Wickwire-Spencer Steel Division of the Colorado Fuel and Iron Corporation makes steel for wire production. In 1945 they changed their open-hearth furnaces from producer-gas to fuel-oil firing, and an account is given of the experience gained from using the new fuel.

Drying Stopper Rods. (Steel, 1946, vol. 119, Sept. 2, pp. 96-97). A brief description is given of an oven for drying ladle stopper rods. The oven holds 69 rods in the vertical position, and, when 20 rods/day are used, each one has a drying time of two or more days at about 350° F.

Duplexing. N. F. Dufty. (Iron and Steel, 1946, vol. 19, Sept., pp. 513-515). Three ways of making steel with the acid Bessemer converter in conjunction with the basic open-hearth furnace are briefly described, and it is shown that this duplex process has several advantages, especially when the price of heavy melting scrap is high; the capital outlay on a tons per hour basis is relatively low.

The Development of the Industrial Vacuum Furnace. W. Hessenbruch and K. Schichtel. (Zeitschrift für Metallkunde, 1944, vol. 36, June, pp. 127-130). The development of vacuum furnaces in the last twenty years is traced. Originally used in the laboratory for 0.5-kg. melts, their size has increased from small brick-lined resistance furnaces, through the low-frequency units, to the modern high-frequency type taking a 5-ton charge. This development is due mainly to W. Rohn. The furnace is used chiefly for preparing special alloys, particularly from easily oxidized components. They are not often used for melting steel.

Distribution of Sulphur between Metal and Slag from the Viewpoint of the Ionic Nature of Slag. A. Samarin, M. Temkin, and L. Shvarzman. (Acta Physicochimica U.R.S.S., 1945, vol. 20, No. 4, pp. 421-440). Consideration of the equilibrium of desulphurization on the basis of the reaction : $\text{FeS}_{\text{in liquid Fe}} + \text{CaO}_{\text{in slag}} = \text{FeO}_{\text{in slag}} + \text{CaS}_{\text{in slag}}$ does not lead to satisfactory results, but the conception of perfect ionic solutions enables the equilibrium between slag and metal to be treated on the basis of the ionic nature of slags. Computations of the equilibrium constant K_s by the equation

$$\frac{a_{\text{Fe}^{++}}a_{\text{S}^{--}}}{x'_s} = K_s$$

(where $a_{\text{Fe}^{++}}$ and $a_{\text{S}^{--}}$ are the activities of Fe^{++} and S^{--} ions in slag respectively, and x'_s is the weight percentage of sulphur in the metal) demonstrates a constancy of K_s for slags of widely varying composition, including slags consisting almost entirely of FeO , of almost pure CaO , containing various amounts of SiO_2 , as well as slags with additions of CaF_2 and CaCl_2 . The data from plant investigations are in fair agreement with those from laboratory researches.

FORGING, STAMPING, AND DRAWING

(Continued from pp. 94 A-95 A)

Forging Operations. J. A. Over. (Iron and Steel Engineer, 1946, vol. 23, Aug., pp. 64-67). Progressive die-forging, using gravity drop hammers and steam hammers, is described and illustrated.

"Eumuco" Shell Forging Press Usage. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 668: H.M. Stationery Office). Descriptions are given of the old horizontal-type and the new vertical-type "Eumuco" shell-forging presses and of an electric-hydraulic upsetting machine for bars up to 30 mm. in dia.

The Forging Process from a Hydrodynamic Point of View. V. Tatarinov. (Steel Processing, 1946, vol. 32, July, pp. 446-447, 459). Equations are developed for calculating the power necessary to overcome the resistance of material to forging. Three examples of their use are given. The first relates to the forging of axles and shafts, the second to the stamping of a cylinder for an air-motor, and the third to drawing a round bar through a blanking ring.

Designing, Drafting and Using Press Tools. C. W. Hinman. (Steel Processing, 1946, vol. 32, July, pp. 441-445). A description is given of the design of pressing dies and the sequence of five operations in the manufacture of a complicated part out of steel strip $\frac{1}{8}$ in. thick.

Recent Developments in Tube Reducing. G. B. Coe. (Iron and Steel Engineer, 1946, vol. 23, Aug., pp. 76-78). The latest type of tubing-drawing machine is described and the reductions which can be obtained in some machines of different size are given.

German Bright Steel Bar Industry. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 618: H.M. Stationery Office). An account is given of German methods of manufacturing bright-drawn steel bars. No methods seen in Germany were superior to ordinary British practice.

The Pros and Cons in Wire-Drawing Dies. (Wire Industry, 1946, vol. 13, Sept., p. 505). The relative

merits of wire-drawing dies made of carbon steel and tungsten carbide are discussed, with notes on the differences in design necessary for the two materials. The advantages of lime as a lubricant are also considered.

Computation of Pulling Force and Stress Distribu-

tion in Wire Drawing. T. Poeschl. (Metallwirtschaft : Engineers' Digest, 1945, vol. 6, Dec., pp. 315-318; Wire Industry, 1946, vol. 13, Sept., pp. 501-502). In this mathematical treatise expressions are developed for calculating the stresses and forces involved in the drawing of wire.

ROLLING-MILL PRACTICE

(Continued from pp. 95 A-96 A)

Automatic Acceleration for D.C. Motors. E. J. Posselt. (Iron and Steel Engineer, 1946, vol. 23, Aug., pp. 83-90). With magnetic controllers for accelerating direct-current motors, sections of the resistor are usually by-passed in steps by a number of accelerating contactors. New methods of automatic control for the accelerating contactors are described and discussed.

Steel Rolling Mills. A. Poole. (British Engineering Export Journal, 1946, vol. 29, Aug., pp. 189-195). Heavy and medium rolling-mill equipment of modern British design is described and illustrated.

Grooved Tramway Rails Rolled in Australia. (B. H. P. Review, 1946, vol. 23, June, pp. 4-6). An account is given of the steps leading up to the rolling of the first grooved tramway rails at the Kembala Works of Australian Iron and Steel, Ltd. The design problems are indicated and the sequence of passes is shown. The rails are rolled in a 36-in. mill comprising three 2-high stands.

Developments in the Production and Use of Sheet Metals. A. McLeod. (Transactions of the Society of Engineers, 1946, vol. 37, Jan.-June, pp. 25-36). Descriptions are given of the two-high rolling of sheets from individual sheet bars and the continuous rolling process, and the advantages of the latter are pointed out. Deep-drawing tests and the study of the surface conditions are considered. The need for a new method of specifying thickness and difficulties in connection with size tolerances and bend allowances are discussed.

Methods of Calculation Used in Rolling Mill Practice. J. H. Mort. (Sheet Metal Industries, 1946, vol. 23, Aug., pp. 1511-1514; Sept., pp. 1713-1718). Calculations relating to the raw material required to fulfil orders received by tinplate, sheet, and broad strip mills are explained.

Cemented Carbide Strip Mill Rolls. (Iron Age, 1946, vol. 158, Sept. 5, p. 61). Solid cemented-carbide rolls (of Kennametal) for the cold-rolling of steel strip have been made. It is claimed that the rolls have a longer life before grinding is necessary, that thinner and harder steels can be rolled satisfactorily, and that a higher accuracy of gauge can be maintained.

German Cold-Rolled Strip Industry. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 681 : H.M. Stationery Office). This is a report on visits to German works to investigate current German practice for producing cold-rolled steel strip in all commercial qualities, and to examine any technical developments in their methods. Special attention was given to hardened and tempered strip, and to clad strip with particular reference to edge dressing.

Cold Strip Rolling. (Electrical Review, 1946, vol. 139, Oct. 18, pp. 599-602). The pickling plant and continuous cold-rolling mills for finishing hot-rolled strip at the works of John Summers and Sons, Ltd., Shotton, are briefly described with numerous illustrations.

The Production of Railway Wagon Wheels and Tyres. (Machinery, 1946, vol. 69, Sept. 26, pp. 385-393). The rolling-mill practice employed at the works of Taylor Bros. & Co., Ltd., Manchester, in the manufacture of railway wagon wheels and tyres is described.

Rolling-Mill Drives. A. S. Wallis. (British Engineering Export Journal, 1946, vol. 29, Sept., pp. 322-330). Some recent improvements in electric drives and controls for rolling mills are described and illustrated.

Design of Mill Tables. J. G. Meenan. (Iron and Steel Engineer, vol. 23, Aug. pp. 53-59). Problems in the design of rolling-mill tables are discussed with special reference to blooming and slabbing-mill tables.

Rail Straightening with a Horizontal-Type Press. P. H. Gast. (Iron and Steel Engineer, 1946, vol. 23, Aug., pp. 91-94). A horizontal-type rail-straightening press of the author's own design is described. This is equipped with adjustable gag-blocks and anvils having relatively broad faces. It is designed so that the pressures are applied in line with both the transverse and vertical axis, and in such a manner that neither the flange nor the head of the rails will be injured during the straightening.

Roll Turning. (Iron and Steel, 1946, vol. 19, Sept. p. 506). A description is given of a new heavy-duty lathe for turning rolls. It will take rolls up to 24 in. in dia. and 8 ft. in length.

PYROMETRY

(Continued from p. 8 A)

Development of the Measurement of Open-Hearth Bath Temperatures. (Industrial Heating, 1946, vol. 13, Apr., pp. 682-685, 698). A description is given 1946—ii.

of the Collins-Oseland temperature-measuring equipment for open-hearth furnaces. This consists of a double-walled tube with a photo-electric cell at one

end connected to amplifying and recording instruments. The open end of the tube is thrust through the slag into the steel bath and air is blown through to keep the end clear.

A Radiation Pyrometer for Open-Hearth Bath Measurements. H. T. Clark and S. Feigenbaum. (American Institute of Mining and Metallurgical Engineers: Technical Publication No. 2031: Metals Technology, 1946, vol. 13, June). A radiation pyrometer, which offers certain advantages with respect to ease of operation, maintenance, and reliability, has been developed and tested under plant conditions. The instrument incorporates a radiation-measuring device mounted inside an open-ended steel tube, which is sighted on the liquid steel. Compressed air keeps the orifice free from molten slag and steel. Tests in the melting shop indicated that the instrument is a practical one for measuring bath temperatures in the open-hearth furnace.

Temperature Measurement of Liquid Steel. D. Manterfield. (Iron Age, 1946, vol. 158, July 25, pp. 52-57). The progress made in the methods of measuring liquid-steel temperatures is reviewed and

full details are given of the construction of the latest type of immersion thermocouple equipment.

Automatic Control of Furnace Temperature and Pressure. (Engineer, 1946, vol. 182, Oct. 11, pp. 321-322). Part of the apparatus for the automatic control of furnace temperature and pressure is described, namely, an electro-pneumatic converter which produces a pneumatic pressure proportional to the thermocouple e.m.f.

The Manufacture of Electrical Measuring Instruments in Germany. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 608: H.M. Stationery Office). The design of a number of German electrical instruments is described. These include potentiometers and thermocouples used for industrial temperature measurement.

Compensating the Effect of the Cold Junction in Thermo-Electric Temperature Measurements. A. Kuntze. (Zeitschrift des Vereines deutscher Ingenieure, 1941, vol. 85, Aug. 16, pp. 703-705). Various methods of cold-junction-temperature compensation in thermocouple temperature-measuring installations are described in detail.

HEAT-TREATMENT

(Continued from p. 96 A)

Electric Furnaces for Tool Heat Treatment. E. F. Watson. (Machinery, 1946, vol. 69, Sept. 19, pp. 361-365). Electrically heated salt-bath furnaces for the heat-treatment of tools are described and recommendations on procedure are made.

Practical Phases of Applying High-Speed Direct Gas Heating. F. O. Hess. (American Gas Association: Industrial Heating, 1946, vol. 13, July, pp. 1122-1136). Illustrated descriptions are given of machines with specially designed gas-burners and conveying equipment for the rapid heat-treatment of large numbers of similar parts.

Equilibrium of Iron-Carbon Alloys with Mixtures of CO-CO₂ and CH₄-H₂. R. P. Smith. (Journal of the American Chemical Society, 1946, vol. 68, July, pp. 1163-1175). By the determination of the carbon content of an iron phase which had been equilibrated with one of a series of gas mixtures, each of constant composition, the following equilibria were measured: (a) CH₄-H₂ mixtures with ferrite at 750° and 7800° C., with austenite at 800° and 1000° C., and with graphite at 800° and 1000° C.; (b) CO-CO₂ mixtures with austenite at 800°, 1000°, and 1200° C., and with graphite at 800° and 1000° C.

The limiting solubility of carbon in ferrite at 750° and 800° C. was found to be 0.020% and 0.0128% by weight respectively, both of which figures are lower than those commonly accepted. Austenite at its lower limit of stability at 800° C. contains 0.319% ($\pm 0.004\%$) of carbon, which is in good agreement with the results of dilatometric measurements. The experimental results permitted direct calculation of the activity of carbon in austenite relative to graphite as unity, and of the heat of solution of graphite in ferrite and in austenite.

In an Appendix (by L. S. Darken and R. P. Smith) an analytical expression, based on statistical considerations, is developed, which reproduces satisfactorily the measurements of the activity of carbon in solid solution in γ -iron and austenite as a function of its concentration.

Salt Baths in the Wire Industry. H. H. Schneider. (Wire and Wire Products, 1946, vol. 21, Aug., pp. 593-596, 615-620, 635). The heat-treatment of wire in salt baths, which includes the patenting, annealing, descaling, and spheroidizing process, is reviewed.

Heating and Cooling of Wire. L. Sanderson. (British Steelmaker, 1946, vol. 12, Aug., pp. 400-404). The conditions for ensuring uniform heating and cooling in the heat-treatment of coils of wire are discussed and recommendations on efficient methods are made.

Bright Hardening. C. E. Peck. (Machinery, 1946, vol. 69, Sept. 12, pp. 321-326). Types of atmosphere for bright-hardening steel and equipment for producing and controlling such atmospheres are discussed. Special attention is given to the controlled heating of the atmosphere in the presence of a catalyst, so that the residual carbon dioxide and moisture contents are very small. To maintain the carbon content of a steel constant during heat-treatment, the carbon potential of the furnace atmosphere must be maintained at a value about equal to that of the steel. An instrument for measuring the carbon potential of a protective atmosphere is described. With this instrument the carbon potential of the atmosphere at various heat-treating temperatures can be evaluated, and these values can be correlated with the equilibrium carbon content of the steel over a wide

range of carbon content. Results of tests show that the carbon potential of a low carbon steel at a high temperature is equal to that of a steel of higher carbon content at a lower temperature. In the hardening of high-speed steels, slightly oxidizing atmospheres are used successfully for the tungsten steels without decarburization, whilst the same type of atmosphere is extremely decarburizing to the molybdenum steels. In any case, at the high hardening temperatures used for high-speed steels, the rates of carburization or decarburization are very rapid, so that it is important that the atmosphere is virtually in chemical balance with the steel.

Induction Heating. R. A. Neilson. (Pacific Coast Electrical Association: Iron and Steel, 1946, vol. 19, Sept., pp. 537-539). Simple formulæ are developed for calculating the optimum frequency to apply for the induction-heating of bars to different depths from the surface.

High-Frequency Generator for Industrial Heating. (Machine Shop Magazine, 1946, vol. 7, Sept., pp. 80-83). A brief description is given of a 25-kW. high-frequency generator for the eddy-current heating of metals or the dielectric heating of non-conductors.

Selective Carburizing by the "Mill-Scale" Method.

R. B. Seger. (Heat Treating Hints: Steel, 1946, vol. 119, Aug. 26, p. 76). A method of preventing the carburization of the surface of the bore of gear-wheels is described. A convenient number of the gears are stacked on a long bolt provided at each end with a washer larger than the diameter of the base. The inside of the assembly is filled up with mill-scale before tightening the nut on the top washer. The stack of gears is then placed in the gas-carburizing furnace.

Heat-Treatment of Grey Cast Iron for Relief of Internal Stresses. P. A. Russell. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 80, Sept. 5, pp. 3-9). An investigation is reported the purpose of which was to determine the relief of internal stresses in high-duty cast iron which could be obtained by heat-treatment. Time, weathering, and machining all relieve internal stress to some extent, but substantial relief can be obtained only by heat-treatment. For high-duty irons with a pearlitic matrix the following treatment is recommended after rough-machining: (1) Heat slowly to 570-600° C.; (2) hold long enough for the whole charge to be uniformly heated; and (3) cool slowly to 300° C. max., preferably to 100° C. Acicular, or partly acicular, irons require special consideration.

WELDING AND CUTTING

(Continued from pp. 96 A-97 A)

Oxy-Acetylene Welding. F. Clark. (Journal of the Institution of Production Engineers, 1946, vol. 25, Sept., pp. 229-261). A comprehensive account is given of the equipment and techniques for the oxy-acetylene welding of ferrous and non-ferrous metals.

Eutectic Low-Temperature Welding. R. D. Boyle. (Australian Welding Institute: Australasian Engineer, 1946, Aug. 6, pp. 71-73). A gas-welding process is described in which the welding rod forms an alloy with the parent metal at a temperature well below the melting point of the rod. Eutectic alloy rods for repairs to cast iron with a bonding temperature in the 354-600° F. range have been developed.

Induction Brazing Carbide Tips to Tools. (Machinery, 1946, vol. 69, Oct. 10, pp. 449-450). Fittings for facilitating handling and increasing the production of induction-heating machines are described. They consist of a tool holder for brazing tungsten-carbide tips to carbon-steel shanks, and a magnetic chuck for holding drills.

Factors Controlling the Strength of Brazed Joints from Final Report N.R.C. 560. C. Rhyne, jun. (Welding Journal, 1946, vol. 25, July, pp. 599-611). This report gives the results of tests of the strength of furnace-brazed joints in steels S.A.E. 4130 and 1010 with copper as the brazing metal. The former steel contains chromium and molybdenum, and the latter is a plain carbon steel. The dominating factor contributing to the strength of the joint is shown to be the degree of deformation of the parent metal at the moment of the failure of the bond. Factors such as finish, clearance, atmosphere, and time, within the

limits ordinarily used, do not have a great effect on the strength of joints in tubes.

Effect of Metallurgical Changes Due to Welding upon the Fatigue Strength of Carbon-Steel Plates. Progress Report No. 1. (Welding Journal, 1946, vol. 25, Aug., pp. 425-S-433-S). The results of fatigue tests and hardness surveys on welded specimens of $\frac{3}{8}$ -in. mild steel plate are presented and discussed. The maximum hardness of 193 Vickers developed in the heat-affected zone was not excessive, as it was only 51 Vickers units above the average hardness of the base metal. The large grains of the heat-affected zone of the single- and double-bead welds were about 2-3 times larger than those in the heat-affected zone of a butt weld in similar plate. The fatigue tests on machined and polished specimens were the only ones of value in judging the effects of welding on fatigue strength. These specimens consisted of plates without welds, plates with a bead on one side, and plates with beads on both sides. The fatigue strengths of these groups had relative values of 1.00, 0.955, and 0.905 respectively.

This work was carried out in the Engineering Experiment Station of the University of Illinois.

Effect of Metallurgical Changes Due to Welding upon the Fatigue Strength of Carbon-Steel Plates. Progress Report No. 3. (Welding Journal, 1946, vol. 25, Aug., pp. 433-S-450-S). Fatigue and hardness tests were made on plain and on welded specimens of $\frac{3}{8}$ -in. plates of two steels, one a 0.27%-carbon steel and the other a Bessemer steel containing 0.064% of carbon. For all specimens with welds the ultimate tensile strength was greater than that of plates with-

out welds, except for one series. The average fatigue strength of the welded specimens of both steels was not significantly different from the average fatigue strength of the corresponding plain specimens.

Residual Stresses in Intersecting Butt Welds. E. P. DeGarmo, J. L. Meriam, and F. Jonassen. (Welding Journal, 1946, vol. 25, Aug., pp. 451-S-463-S). This paper is one of a series covering work done at the University of California to study the residual stresses in intersecting butt welds in 1-in. steel plates which occur in shipbuilding. The conclusions reached were: (1) The magnitude and general pattern of the residual stresses in large structures (up to 27×57 ft.) can be obtained in panels as small as 4×6 ft. (2) In butt welds the longitudinal residual stresses along the centre line of the weld attain a magnitude of about 47,000 lb./sq. in., and the transverse residual stresses are usually less than 10,000 lb./sq. in. (3) When two butt welds intersect, the residual stresses at the point of intersection are no higher than at other positions in the welds. (4) In assembling several large steel plates into a large panel, the residual stresses after welding the joints from end to end are only a very little greater than when the welding is begun at the mid-point of the joints and runs to the ends.

The Effect of Weld Length upon the Residual Stresses of Unrestrained Butt Welds. E. P. DeGarmo, J. L. Meriam, and F. Jonassen. (Welding Journal, 1946, vol. 25, Aug., pp. 485-S-487-S). A series of butt welds were made joining 1-in. steel plates of different lengths up to 4 ft. and the residual longitudinal stresses were determined. For welds up to about 20 in. long the value of the maximum stress increased with the length of weld. With longer welds the residual stress rose from zero at the ends to a maximum at about 10 in. from each end. Throughout the remainder of the length the stresses were fairly constant at the maximum value.

Effect of Temperature Gradients upon the Introduction of Residual Stresses in Weldments or Steel Castings. J. R. Stitt. (Ohio State University, Engineering Experiment Station News: Welding Journal, 1946, vol. 25, Aug., pp. 487-S-488-S). Specifications are quoted to show that there is no agreement on the cooling rate to adopt after stress-relieving welded steel pressure vessels and castings at 1100° F. for 1 hr. Calculations are presented in this paper which prove that, if there is a temperature difference of 170° F. between any two points during cooling, stresses up to the yield point will be set up.

Crack Sensitivity of Chromium-Nickel Stainless Weld Metal. R. D. Thomas, jun. (Metal Progress, 1946, vol. 50, Sept., pp. 474-477). A summary is presented of experience gained regarding the crack-sensitivity of stainless steel weld metal. Weld metal containing ferrite is less susceptible to cracking than fully austenitic compositions. The following equation has been developed by F. K. Bloom for determining whether ferrite is present from the composition of the weld metal:

$$\frac{(\text{Cr} + 2\text{Mo} - 16)^2}{12} = \frac{\text{Mn}}{2} + 30(0.10 - \text{C}) + 11.$$

If the percentage of nickel in the metal is below this value, the structure will probably be partially ferritic; if it is higher, it will probably be entirely austenitic. Other things being equal, an electrode coating containing titania is more likely to produce a crack-sensitive weld than is one with a lime-type coating.

Poke Welding of Stainless Steel Cold Storage Sheathing. R. K. Waldvogel. (Welding Journal, 1946, vol. 25, Aug., pp. 738-744). A description is given of a method of resistance welding which was developed for joining the stainless-steel sheets which form the casing of refrigeration chambers in ships. In this form of welding a manually operated gun forms one electrode which is pressed against the sheet metal at the points where it is desired to make the spot welds.

Welding the Stainless Alloys in the "Shooting Star" Jet Engine. W. J. Campbell. (Steel Processing, 1946, vol. 32, July, pp. 431-435). **Welding Jet Engine Parts.** W. J. Campbell. (Iron Age, 1946, vol. 158, Sept. 6, pp. 46-49). The techniques developed for welding columbium-stabilized stainless steel and other alloys used in the construction of jet engines are described.

Welding the Stainless Steels. J. L. Filbert. (Welding Journal, 1946, vol. 25, July, pp. 642-644). The characteristics of austenitic and ferritic stainless steels and of the martensite-forming stainless steels are enumerated and recommendations on the appropriate welding procedures are made.

Fusion Welding of Sheet Metal. J. M. Diebold. (Welding Journal, 1946, vol. 25, Aug., pp. 724-732). The advantages and characteristics of several methods of welding steel sheet are outlined and discussed. These methods include oxy-acetylene, atomic hydrogen and Heliarc welding, the Unionmelt process, and several forms of electric welding.

The Spot Welding of Mild Steel Sheet of Varying Carbon Contents. W. S. Simmie. (Sheet Metal Industries, 1946, vol. 23, Sept., pp. 1777-1784). An investigation to determine the optimum conditions for the spot-welding of 16 S.W.G. sheets of steels containing 0.16%, 0.246%, and 0.292% of carbon is reported. The best welds were obtained with a welding pressure of 10,000 lb. per sq. in. and post-heating the welds for 10 cycles (at 50 cycles/sec.) after welding.

The German Electrically Welded Steel Tube Industry. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 674: H.M. Stationery Office). An account is given of the methods employed at 19 German works manufacturing welded steel tubes, more particularly tubes made from electrically butt-welded strip.

Cracking of Welded Gas Mains. L. Reeve. (British Welding Research Association's Symposium on Metallurgy of Steel Welding: Transactions of the Institute of Welding, 1946, vol. 9, Aug., p. 133). See Journ. I. and S.I., 1946, No. I., p. 45 A.

Investigation of Failures in a Welded Bridge. H. Busch and W. Reuleke. (Welding Journal, 1946, vol. 25, Aug., pp. 463-S-466-S). This is an abridged English translation of a paper which appeared in Stahl und Eisen, 1942, vol. 62, Jan. 22,

pp. 66-72 (*see* Journ. I. and S.I., 1942, No. II, p. 21 A).

Electro-Physics of the Welding Arc. L. H. Orton. (British Welding Research Association's Symposium on Metallurgy of Steel Welding: Transactions of the Institute of Welding, 1946, vol. 9, Aug., pp. 131-133). *See* Journ. I. and S.I., 1946, No. I., p. 45 A.

Mineral Constituents of Arc-Welding Slags. R. C. Vickery. (Metallurgia, 1946, vol. 34, Aug., pp. 177-180). A study is made of the reactions at high temperatures of the major constituents (FeO , MnO , TiO_2 , and SiO_2) of arc-welding electrode coatings. The experimental procedures were such as to approach closely the conditions of slag formation during welding, and the samples of slag thus obtained were examined petrographically. A sequence is suggested for the interaction of the electrode coating constituents, and observations are made on the practical applications of the findings.

Properties of Lime Ferritic Electrodes. O. T. Barnett. (Steel, 1946, vol. 119, Aug. 19, pp. 96-97, 128-130). Particulars are given of a new type of welding electrode with a heavy coating, the principal ingredients of which are calcium carbonate and calcium fluoride. It is claimed that high-carbon steel, cast steel, enamelling steel, and cast iron can be readily welded with this new electrode.

Applications of Lime Ferritic Electrodes. O. T. Barnett. (Steel, 1946, vol. 119, Aug. 26, pp. 80-86). Examples of successful welding work on high-carbon and alloy steels with the electrodes referred to in the preceding abstract are described.

Arc-Welding Cast Iron. (Steel, 1946, vol. 119, Sept. 9, p. 128). Particulars are given of "Ni-Rod,"

a nickel electrode for welding cast iron, which reduces the need for special treatment of the casting before and after welding.

Metallurgy for Welders. II. D. Llewellyn. (Welding, 1946, vol. 14, Sept., pp. 427-430). Continuation of a series of articles (*see* p. 74 A). In this part simple definitions for the terms used in specifying the properties of metals are given.

A Review and Summary of Weldability Testing Carbon and Low Alloy Steels. G. L. Luther, C. E. Jackson, and C. E. Hartbower. (Welding Journal, 1946, vol. 25, July, pp. 376-S-396-S). This is a review of the literature and a summary of all the weldability tests which the authors consider to be applicable in the construction of ships' hulls. The bibliography contains 53 references.

Standard Welding Symbols. (Welding Journal, 1946, vol. 25, July, pp. 612-641). The standard welding symbols here presented have not been approved by the American Welding Society. They have been prepared by the A.W.S. Committee on Symbols, and are proposed as a revision of the Society's standard entitled "Welding Symbols and Instructions for their Use". They are now published so as to elicit comments and suggestions.

Economical Method of Flame-Cutting Cast Iron. (Steel, 1946, vol. 119, Sept. 16, pp. 115-116). The equipment and technique for cutting cast iron with a special oxy-acetylene burner are described.

Flame Cutting and Welding in Bulldozer Manufacture. H. H. Washbond and O. F. Wilkinson. (Iron Age, 1946, vol. 158, Sept. 12, pp. 56-59). It is shown how oxy-acetylene cutting and electric welding are applied in the fabrication of bulldozer parts.

CLEANING AND PICKLING OF METALS

(Continued from pp. 75 A-76 A)

Processing and Fabrication of Stainless Steel Sheet and Plate Products. Part VI. H. S. Schaufus, W. H. Braun, and I. C. Clingan. (Steel Processing, 1946, vol. 32, June, pp. 372-375, 399). Continuation of series of articles (*see* p. 52 A). Mechanical, chemical, and electrolytic methods of cleaning and polishing stainless steel are described.

Polishing Methods and Technique. L. Mable. (Journal of the Electrodepositors' Technical Society, 1945-46, vol. 21, pp. 103-112). The materials, machinery, and technique for the polishing of ferrous and non-ferrous metals are described with notes on the selection of operators for different classes of work.

Metal Polishing. R. MacNair. (Sheet Metal Industries, 1946, vol. 23, Sept., pp. 1746-1750). General

recommendations on the art of polishing metals with abrasives are made with data on polishing speeds and the best abrasives to use for different metals.

Vapour Degreasing. G. Black. (Materials and Methods, 1946, vol. 24, July, pp. 95-97). The properties of trichlorethylene and perchlorethylene as solvents for vapour degreasing are discussed, and the advantages and limitations of the vapour process are considered.

Glycerine: Friend of the Wire Worker. G. Leffingwell and M. A. Lesser. (Wire and Wire Products, 1946, vol. 21, Aug., pp. 604-605, 635). The literature on the use of glycerine in cleaning solutions and fluxes, and on synthetic alkyd resin for coating and insulating wire, is reviewed.

COATING OF METALS

(Continued from pp. 76 A-77 A)

Protective and Decorative Coatings for Metals. A. F. Brockington. (Sheet Metal Industries, 1946, vol. 23, July, pp. 1355-1362; Sept., pp. 1751-1755). A general review of methods of coating and plating metals and obtaining decorative finishes is presented.

The Influence of Anodes in Plating Processes. S. R. Goodwin, G. M. Bechtold, and H. A. Bechtold. (Journal of the Electrodepositors' Technical Society, 1945, vol. 20, pp. 105-118). The requisites of a good anode and the characteristics of the following

types of anode which are commonly used in the plating industry are explained: the plate anode, the oval section anode, the ball anode, and the gear anode.

Chlornaphthalene Wax for Stopping-Off in Electrodeposition Practice. Its Advantages and Limitations. C. W. Richards. (Journal of the Electrodepositors' Technical Society, 1945, vol. 20, pp. 155-164).

Electrography Applied to the Examination of Electrodeposits. H. D. Hughes. (Journal of the Electrodepositors' Technical Society, 1945, vol. 20, pp. 17-30). The apparatus and procedures for the electrographic method of identifying electrodeposits and examining them for imperfections are described. This method consists of impregnating a pad of folded paper with a suitable reagent, applying the pad to the surface to be tested, and passing a current through the metal and pad by touching the outer surface of the pad with a graphite rod, which is made the cathode, whereupon a coloured spot is formed on the pad.

Pressing Technique as a Preliminary to the Production of Good Electrodeposits. J. D. Jevons. (Journal of the Electrodepositors' Technical Society, 1945, vol. 20, pp. 93-104). This paper aims at giving the electrodepositor a short description, first, of some of the defects or conditions in metal sheet and strip which cause trouble during plating and, secondly, of press-shop operations and the manner in which these influence the product from the viewpoint of the electrodepositor to whom they will be passed.

Precision Metal Parts Produced by Electroforming. H. R. Clauser. (Materials and Methods, 1946, vol. 24, July, pp. 112-116). A detailed account is given of the electroforming process. This is a particular application of the plating process in which a die or mould is made from a master pattern of the part to be formed. This die or matrix is plated to the required thickness in a bath; after removal from the bath the deposited metal is separated from the matrix and forms an exact duplicate of the master pattern.

Analysis of Electroplating "Strike" Solutions. (Steel, 1946, vol. 119, Aug. 5, pp. 124-125, 141, 144). Apparatus and procedure are described for a new method of routine production control in the deposition of metal from strike solutions.

Plating Rack Coatings. L. A. Critchfield. (Monthly Review of the American Electroplaters' Society, 1946, vol. 33, Feb., pp. 152-157, 191). The advantages of coating plating racks are pointed out and methods of coating them with plastic tape wax, rubber, and synthetic resin are described.

Economics of Electroplating. T. F. O'Connor. (Metal Industry, 1946, vol. 69, Aug. 2, pp. 97-100; Aug. 16, pp. 140-142). Having ascertained that a range of current densities is permissible for the mass production of electroplated articles, it is possible, when certain other factors are known, to calculate one current density which will determine the optimum size of plant and the lowest operating cost per article. These calculations are explained in this paper.

Nickel Plating on Steel by Chemical Reduction. A. Brenner and G. E. Riddell. (Journal of Research of the National Bureau of Standards, 1946, vol. 37,

July, pp. 31-34). A process has been developed for the production of adherent nickel deposits of good quality on steel without the use of an electric current. The deposition is brought about by the chemical reduction of a nickel salt with hypophosphites in a hot ammoniacal solution. The reaction is catalytic and, under the prescribed conditions of concentration and pH, no reduction occurs in the solution unless certain metals, such as steel or nickel, are introduced into the bath. The reduction then occurs only at the surface of the immersed metal with the production of a coating of nickel of 96-97% purity.

High Speed Zinc Plating. A. E. Carlson and M. J. Krane. (Monthly Review of the American Electroplaters' Society, 1945, vol. 32, Oct., pp. 1022-1026). A procedure for the rapid electrolytic deposition of zinc on steel, using a zinc fluoborate bath, is described.

Hot Air Dryer Doubles Galvanizing Output. W. G. Imhoff. (Iron Age, 1946, vol. 158, Aug. 8, pp. 54-55). A brief description is given of a drying table for drying out buckets and other articles between pickling and galvanizing operations. The table has a lattice top through which rises hot air heated by gas burners below.

End-Point Indication of the B.N.F. Jet Test for Measurement of Thickness of Zinc Coatings on Steel. S. G. Clarke. (Journal of the Electrodepositors' Technical Society, 1945, vol. 20, p. 75). In the British Non-Ferrous Metal Research Association jet test for measuring the thickness of zinc coatings difficulties may arise because the perforation point is not clearly visible. One or two drops of the following solution applied on the spot will give a clear indication of perforation: Potassium ferri-cyanide 20 g., concentrated hydrochloric acid 20 c.c., with water to make 100 c.c.

Lead-Tin Alloy Plating. A. E. Carlson and J. M. Kane. (Monthly Review of the American Electroplaters' Society, 1946, vol. 33, Mar., pp. 255-261). Methods for the electrolytic deposition of lead-tin alloys (with any desired amount of tin in the 5-60% range) are described with details of procedures for determining the lead and tin contents of the solutions used.

Aluminum Dipcoated Steel. (Materials and Methods, 1946, vol. 24, July, pp. 90-94). Steel strip dip-coated with aluminium is now available in the United States. The thickness of the coating is about 0.001 in. and its weight is 0.25 oz./sq. ft. The material, its properties, and some of its applications are described. It can be heated up to about 900° F. before discolouration begins.

Phosphate Processes as a Pre-Treatment for Metal Finishing. H. A. Holden. (Sheet and Strip Metal Users' Technical Association: Sheet Metal Industries, 1946, vol. 23, Aug., pp. 1539-1546). A detailed description of the Bonderizing process of forming a phosphate coating on steel is given. A process for phosphatizing zinc is also briefly described.

Neoprene Linings for Chemical and Corrosion Protection. G. A. Ronsen. (Corrosion and Material Protection, 1946, vol. 3, June-July, pp. 8-11). The methods employed by an American company for

coating metal parts with Neoprene and examples of chemical equipment lined with this synthetic rubber are described.

Worn Shafts. Building up by Metal Spraying. S. Staton. (Iron and Steel, 1946, vol. 19, Sept., pp. 511-512). A detailed description is given of the equipment and technique for building up worn shafts by metal spraying.

Relation of Enameling Iron Preparation and Accessory Conditions to Copperhead-Type Defects. W. H. Pfeiffer and R. S. Sheldon. (Journal of the American Ceramic Society, 1946, vol. 29, Sept., pp. 235-239). The tendency for the defect known as "copperhead" to occur in blue ground-coat enamels is shown to be related to residual iron salts formed on the surface of sheets of enamelling iron in sulphuric-acid pickling. The ferrous sulphate generated in the pickling oxidizes and hydrolyses readily into compounds which are not soluble in the cyanide neutralizer. These effects may be retarded by keeping the solutions between the sulphuric acid and the neutralizer slightly acid, by reducing the time in these solutions, and by reducing the time of exposure to air when the work is transferred from one solution to the other. The determinations of these conditions and the establishment of satisfactory procedures in the production process are described.

Stiffening Effect of Porcelain Enamel on Sheet Iron. D. S. Wolford and G. E. Selby. (Journal of the American Ceramic Society, 1946, vol. 29, June, pp. 162-175). Bend tests were made on small flat panels of 18-28 gauge sheet iron coated on both sides with porcelain enamel in thicknesses ranging from 0.004 to 0.025 in. The stiffening effect of the coating was evaluated. Methods are described by which the bending, tensile, and compressive properties of the enamel coating and the sheet iron can be separately determined.

Production of Cast-Iron Porcelain Enamelled Baths in Germany. (British Intelligence Objectives Sub-Committee, 1945, Final Report No. 437: H.M. Stationery Office).

Report on Anti-Fouling Research, 1942-44. Marine Corrosion Sub-Committee. (Iron and Steel Institute, 1946, this Journal, Section I.). The present report is an endeavour to collect together the salient features of the anti-fouling work of the Marine Corrosion Sub-Committee up to 1944. The work has been greatly expanded since the completion of the First Report (*see* Journ. I. and S.I., 1943, No. I, p. 339 p), and it is impossible to make this account exhaustive.

The technique of exposure tests on anti-fouling compositions is described. Patch tests of a minimum area (12 × 8 in.) on a larger panel are employed for comparative work. The test patches are arranged at random to eliminate systematic errors. "Seasoned" panels, painted with the best possible protective system, are used. The assessment of fouling on the panels is carried out by examination in a sea-water tank, emphasis being laid on the kinds of organism present rather than on the quantity. Suitable dates for commencing tests are in spring for short-period tests and in autumn for long-period tests. The sequence of settlement of fouling organisms is not a

causal chain but is largely determined by the seasonal occurrence of the settling stages of each organism. Sequences may, however, develop on a toxic surface owing to gradual decrease in toxicity. Emphasis is laid on the importance of *qualitative* fouling assessments which determine the *time of breakdown* of the anti-fouling protection; quantitative measures, though valuable for some purposes, are used more as indicators of *external factors* in the environment. The seasonal settlement of fouling forms at Millport is described briefly, and is compared with conditions elsewhere in the British Isles. The susceptibility of fouling organisms to poisons varies considerably and can be employed to determine grades of anti-fouling efficacy. The part played by bacterial slime in fouling is discussed at some length. It is not a necessary precursor of fouling, but is highly resistant and readily developed on rosin-containing coatings. It therefore tends to develop early and may influence subsequent settlements to a limited extent. This slime does not serve as a cumulative store of poison over a toxic paint.

The principal features of diatom, seaweed, and animal fouling organisms are described, particular attention being paid to such factors as season of occurrence, mode of settlement and attachment, and relative susceptibility to poisons. A brief analysis of the factors concerned in the fouling on ships' bottoms is accompanied by a summary of the results of a preliminary study of samples from 30 voyages to tropical waters. The mode of action of anti-fouling coatings is demonstrated by an experiment giving a toxic border around a patch of anti-fouling composition. The toxicity appears to be produced by a thin layer of poisonous sea-water immediately over the paint surface. The loss of poison from the paint into this toxic layer is correlated with chemical analysis of the copper and mercury content of sea-water in which painted panels are immersed; this process is known as the leaching test. Under the experimental conditions prescribed, a rate of loss of copper of 10 µg./sq. cm./day in the laboratory test is an adequate indicator of successful anti-fouling properties. In the presence of mercury this rate of loss of copper may be lower. The leaching technique is described and suitable methods for the estimation of copper and mercury in the leachate are presented. Preliminary studies of the effect on the laboratory leaching rate of varying the paint constituents are given. The most important factor is the resin component. In a rosin/linseed-oil varnish, replacement of the rosin by ester gum, acid or neutral synthetic resins, waxes, lanolin, bitumen or (by decreasing the rosin content) drying oil, all produce a fall in the copper leaching rate, which in a rosin-oil varnish is approximately proportional to the copper content of the paint film. Mercuric oxide also lowers the copper leaching rate from a cuprous-oxide paint. The practical significance of this leaching test is at present limited to the prediction of success or failure of the anti-fouling properties of a formulation. It has only a very limited value in estimating the effective anti-fouling life, since the leaching slides are stored in laboratory tanks and lose poison less rapidly than in the sea. Methods

of overcoming this difficulty are being explored and the existing technique is a useful laboratory tool in working out practical paint formulations. Experiments on the use of organic poisons in anti-fouling compositions are described. Certain organic arsenicals, a number of organic sulphur compounds, and organo-mercurial derivatives offer possibilities of development, but a large number of highly toxic compounds fail as anti-fouling agents. This failure is very largely correlated with high solubility in the non-polar solvents.

A description of a promising development in an aqueous cementiferous composition using organic poisons as anti-fouling agents is given. Compositions of this type open up the possibility of applying a single-coat system, firmly adherent to wet, rusty, or mill-scale-covered steel, which is adequate for anti-corrosive and anti-fouling purposes, and which may be dried out after long periods of immersion without any deleterious effect.

Action of Antifouling Paints. J. D. Ferry and B. H. Ketchum. (Industrial and Engineering Chemistry, 1946, vol. 38, Aug., pp. 806-810). Maintenance of the leaching rate of anti-fouling paint which contains a high loading of toxic in an insoluble

impermeable matrix depends upon the continuous contact of the toxic particles throughout the paint film. When paints formulated with cuprous oxide and vinylite are extracted either in citrated sea-water in the laboratory or in the open sea, the toxin dissolves and leaves the matrix intact. The rate at which the leaching rate falls during extraction, as well as the total amount of toxin extractable, is sensitive to the proportion of toxin in the paint. This proportion must exceed 30% by volume to make particles below the surface accessible to solvent action. Anti-fouling coatings of this type have the advantage of being effective when applied as a thin film, with good resistance to erosion.

Action of Antifouling Paints. J. D. Ferry and G. A. Riley. (Industrial and Engineering Chemistry, Industrial Edition, 1946, vol. 38, July, pp. 699-701). The solubilities in sea-water of various copper and mercury compounds which have been proposed as anti-fouling toxics cover a very wide range—from 10^{-3} to over 10^5 $\mu\text{g.}$ of metal per c.c. Cuprous oxide has a solubility of 5.4 $\mu\text{g.}$ of copper per c.c., which is high enough to be effective, but not so high that its leaching rate from anti-fouling paints is too difficult to control.

PROPERTIES AND TESTS

(Continued from pp. 97 A-100 A)

A Method for Evaluating Toughness of Steel. S. A. Herres and A. F. Jones. (Metal Progress, 1946, vol. 50, Sept., pp. 462-469). The problem of finding a convenient unit for expressing the toughness of steel is discussed. Data on the relationships between the tensile, impact, and hardness values of steel after various heat-treatments are presented. Ratings which depend largely on the reduction of area in ordinary tensile tests are not reliable criteria of the toughness, or of the ability of a metal to absorb energy before fracture. A better rating would be one based on the Charpy notched-bar impact test made at -40°F. This value should be higher for steels of moderate tensile strength than for steels of higher hardness and strength.

The Calibration of Mechanical Testing Machines. G. L. Brown. (Australian Institute of Metals: Australasian Engineer, 1946, July 8, pp. 37-40). Descriptions are given of methods of calibrating mechanical testing machines. Proving levers, the proving ring, the proving loop, and the Amsler standardizing box are also described.

Low-Temperature Behavior of Ferritic Steels. H. W. Gillett and F. T. McGuire. (Steel, 1946, vol. 119, Aug. 12, pp. 76, 98-104). See Journ. I. and S.I., 1945, No. II., p. 191 A.

Analytical Expressions for Principal Strains. W. T. Thomson. (Journal of Applied Mechanics, 1946, vol. 13, Sept., pp. A-221-A-222). Methods recently developed by G. Murphy and N. J. Hoff enable the graphical evaluation of the principal strains to be made from strains measured along any three intersecting lines. When the two angles between gauge

lines are equal, the principal strains may be determined from simple analytical expressions without reference to the graphical solution.

Internal Friction in Engineering Materials. J. M. Robertson and A. J. Yorgiadis. (Journal of Applied Mechanics, 1946, vol. 13, Sept., pp. A-173-A-182). A new apparatus and technique for measuring the damping capacity of solid engineering materials are described. The vibratory system employed consists of a centrifugal-force mechanical oscillator maintaining resonant vibration in a specimen which is the flexible member of the vibrating system. The energy input to the system is obtained from measurement of the amplitude of the motion and the force amplitude of the oscillator. On the basis of the data obtained with this apparatus empirical relationships are presented for the variation of internal friction with the amplitude of the stress. These relationships are compared with the findings of other investigators.

The Activation Energy of the Recovery of Metals Strengthened by Cold Deformation. G. Masing. (Zeitschrift für Metallkunde, 1944, vol. 36, July, pp. 173-176). The activation energy of the recovery of metals subjected to different degrees of cold deformation has been studied. A quantitative analysis of the results obtained by M. O. Kornfeld, using aluminium specimens, led to the conclusion that the activation energy does not depend on the magnitude of the initial increase in strength, but on the increase at the moment of recovery.

Strain Analysis by Photogrid Method. W. F. Brown, jun., and M. H. Jones. (Iron Age, 1946, vol. 158, Sept. 12, pp. 50-55). Techniques for producing a grid

on parts which are to be tested or subjected to deformation and methods of measuring the amount of strain after deformation are described. The following formula was developed at the Case School of Applied Science for making the emulsion for coating the part: Water 23 parts (by weight), photo-engraver's glue 4 parts, ammonium dichromate 1 part, and ammonium hydroxide $\frac{1}{4}$ part. Celluloid negatives of the grid are prepared and the lines are photographed on to the emulsion using ultra-violet high-intensity radiation.

Stress by Analysis and Experiment. A. J. Sutton Pipard. (Proceedings of the Institution of Mechanical Engineers, 1946, vol. 155, pp. 20-28). An attempt is made to outline the bases of structural analysis when stresses do not exceed the limit of proportionality. The fundamental theories are stated, and the general problems of analysis of "just-stiff" and redundant frameworks are discussed.

Brittle Lacquers. H. Weibull. (Teknisk Tidskrift, 1946, vol. 76, Sept. 21, pp. 921-923). (In Swedish). An account is given of the method of stress analysis, using a brittle lacquer, developed by Maybach Motorenbau G.m.b.H. The calibration of the lacquer on a series of steel-strip test pieces is described and a statistical method of calculating the probability of fracture is explained.

How Rails Break. C. Dinsdale. (Journal of the Permanent Way Institution, 1946, vol. 64, Apr., pp. 46-71). This is a comprehensive discussion of the problem of defective and broken rails. The causes of rail failure are divided into two principal classes. The first covers failures and defects arising from faulty material; in this part ingot defects, rolling defects, and transverse fissures are dealt with. The second class covers the following failures and defects arising from service conditions: (1) Wear, (2) fatigue and impact, (3) rail-end batter, (4) failure in tunnels, (5) corrosion at water troughs, (6) corrosion at wet ash pits, (7) damage by slipping engine wheels, (8) faulty heat-treatment, (9) faulty welding, (10) faulty cutting, and (11) rail corrugation. An appendix sets forth the routine test schedule used in the L.N.E.R. metallurgical laboratory for examining defective rails.

Steel Rails. C. Dinsdale. (Iron and Coal Trades Review, 1946, vol. 153, Sept. 13, pp. 447-454; Sept. 20, pp. 487-494; Sept. 27, pp. 537-547; Oct. 4, pp. 585-591; Oct. 11, pp. 631-638). An account is given of the metallurgical nature of rails and how they fail in service. Part I. describes the evolution of the steel rail, the composition and properties of old and new rails, and includes some notes on British and foreign specifications for rails. Part II. is devoted to the heat-treatment and welding of rails. Part III. deals with the repair of rails by welding and gives a detailed study of the metallography of modern rails. In Parts IV. and V. descriptions are given of many types of rail failure caused by service conditions (see preceding abstract).

Gear Tooth Wear and Failure. (Machinery, 1946, vol. 69, Sept. 12, pp. 329-332). The American Gear Manufacturers' Association has recently adopted a nomenclature standard entitled "Standard for Terms Used in Designating Gear Tooth Wear and

Failure." Its purpose is to avoid misunderstanding between manufacturers and users. In this article these terms are defined and an illustration of each type of wear or failure is given.

An Empirical Approach to the Fatigue-Strength Analysis of Structures. H. W. Foster and V. Seliger. (Journal of Applied Mechanics, 1946, vol. 13, Sept., pp. A-201-A-206). A method of fatigue-strength analysis for fabricated structures, based on laboratory fatigue-test data is proposed.

Hardenability Testing in Material Control. E. H. Snyder. (Steel, 1946, vol. 119, Aug. 26, pp. 72-73, 120-124). The manner in which a company manufacturing gears, bolts, and studs applies the end-quench test to the control of their heat-treatment operations is explained.

Hardenability Test for Quenched and Tempered Steel. E. J. Wellauer. (Steel Founders' Society of America: Iron Age, 1946, vol. 158, Sept. 5, pp. 62-66). The hardenability data obtained on quenched and tempered bars by the end-quench test are discussed, and curves are presented showing the decrease in hardness with increasing tempering temperature. An example is given of the application of such data to the prediction of the tempering temperature required to produce a given hardness in a part of given size.

Effect of Undissolved Carbides on Hardenability. R. J. Hafsten. (Steel, 1946, vol. 119, Aug. 19, pp. 112-114). The effect of undissolved carbides in austenite on the structure obtained after quenching is discussed. Micrographs of specimens of a 1%-carbon steel quenched in oil from 1600° F. are presented. This quench was not rapid enough to produce 100% of martensite, so a small amount of pearlite was present. These pearlite nodules were nucleated at what had been the carbide-austenite interface. Carbides not in solution in the austenite at the moment of quenching result in lower hardenability.

Diamond Hardness Testing. (Metal Industry, 1946, vol. 69, Sept. 13, pp. 223, 226). When the sides of the diamond impression in hardness testing appear curved instead of as straight lines a correction should be applied to the hardness number derived from reading the mean diagonal length. The correction factor derived by T. B. Crow and J. F. Hinsley is explained.

The Formation of Martensite in Iron-Nickel-Cobalt Alloys. K. Schichtel and U. Wilke-Dörfurt. (Zeitschrift für Metallkunde, 1944, vol. 36, June, pp. 147-148). Martensite often appears in a 54/27/19 iron-nickel-cobalt alloy after deformation and heat-treatment; this can be suppressed by the addition of 0.5% of chromium. This tendency to martensite formation appears after annealing at 1250° C., deforming, and tempering at 500° C. The effects of chromium additions on the mechanical and electrical properties of the alloy are given.

Temper Embrittlement of Aircraft Steels. P. A. Haythorne. (Iron Age, 1946, vol. 158, Aug. 29, pp. 51-55). Tension-impact tests and Charpy and Izod impact tests were carried out on specimens of chromium-nickel-molybdenum aircraft steels after heat-treatment and tempering at different tem-

peratures. The greatest loss in impact strength indicated by the Charpy tests occurred after tempering in the 525–675° F. range, whereas the Izod and tension-impact test results were lowest after tempering in the 525–675° F. and 700–835° F. ranges respectively. Existing specifications requiring a minimum tempering temperature of 650° F. appear to be unsatisfactory, and a new form of test relating the ultimate tensile stress to brittleness is required.

The Temper-Brittleness of Steels Containing Chromium, Molybdenum, and Tungsten. G. Vidal. (Iron and Steel Institute, 1946, Translation No. 291). This is an English translation of a paper which appeared in *Revue de Métallurgie, Mémoires*, 1945, vol. 42, May, pp. 149–155. (See p. 33 A).

Heat Treatment of Heavy Cast Steel Sections. P. C. Rosenthal and G. K. Manning. (Foundry, 1946, vol. 74, Aug., pp. 70–75). The hardness, impact strength and microstructure of quenched and tempered steel plates up to 6 in. thick, and the effects of additions of alloying elements were investigated. The shape of a casting imposes a limit to the amount of alloying element which can be added without a prohibitive amount of cracking on quenching. The susceptibility of the steel to temper brittleness increases, in general, with the amount of alloying element added; molybdenum is an exception to this as large additions cause too great a hardness and lead to unmachinable microstructures.

Testing Materials with Supersonic Waves. J. Bick. (Teknisk Tidskrift, 1946, vol. 76, Sept. 28, pp. 937–942). (In Swedish). The theory on which the design of supersonic emitters and receivers for testing materials is based is explained. The testing equipment developed at Tekniska Röntgencentralen in Stockholm and some investigations conducted with it are described.

Supersonic Inspection of Materials. H. R. Clauser. (Materials and Methods, 1946, vol. 24, Aug., pp. 379–384). The principles of supersonic methods of detecting flaws in metals are explained and particulars are given of the Sperry Supersonic Reflectoscope in which the defect reflects the waves back to the surface, and of the Brush Hypersonic Analyzer in which the emitter and receiver are on opposite sides of the metal under test.

Non-Destructive Testing of Metal Parts. R. L. Cavanagh. (Steel Processing, 1946, vol. 32, July, pp. 436–440). A description is given of the magnetic testing apparatus known as the “Der Mont Cyclograph.” The Cyclograph has a frequency range of 3000 to 150,000 cycles, which is controlled by the design of the test coil. The parts to be tested are placed inside a test coil, and its magnetic properties are compared with those of a standard part forming the core of a second coil.

Non-Destructive Testing of Materials. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 609: H.M. Stationery Office). A report is presented on German methods of testing materials by non-destructive methods, with particular reference to: (1) The magnetic method of measuring the austenite in steel as practised in the research laboratories of the Deutsche Röhrenwerke A.G.; (2) the

magnetic methods of flaw detection developed by the Siemens organization; (3) the work done on autofrettage by Dr. Claus at Göttingen; (4) the application of supersonics to non-destructive testing by the Siemens organization; and (5) Menzel's method of degassing metals by supersonic vibration.

Non-Destructive Testing Methods. R. Le Grand. (Machinist, 1946, vol. 90, Sept. 7, pp. 893–916). Brief descriptions are given of the following non-destructive methods of testing; Radiography, gamma-ray inspection; fluoroscopic inspection; X-ray diffraction; magnetic powder inspection; inspection with a fluorescent penetrating fluid; supersonic methods; the Penetron gauge for measuring the thickness of tubes and vessels from one side only; electronic inspection for detecting and recording holes, cracks, and pits in tubes; gauges for film-thickness measurement; spectrographic examination; and magnetic analysis. Simple diagrams showing the principles involved in these methods are presented.

Crack Detection. D. Taylor. (Automobile Engineer, 1946, vol. 36, July, pp. 319–321). The theory of the magnetic-powder method of crack detection is explained and its utility and limitations are discussed.

Effects of Grain Growth Inhibitors in Fine-Grained Steels. J. W. Halley. (American Institute of Mining and Metallurgical Engineers: Steel, 1946, vol. 119, Sept. 2, pp. 98–99, 124). Experiments were carried out in which additions of aluminium, titanium, and zirconium were made to 0.30%-carbon steels so that the effects on the grain-coarsening with subsequent heating could be studied. The highest temperature of grain-coarsening (1800° F.) was obtained in the case of aluminium with an addition of 0.028%. Titanium increased the coarsening temperature continuously up to 0.17% of titanium. Zirconium was less effective in inhibiting grain-coarsening than either aluminium or titanium. The results of tensile and impact tests on the steels are also given.

Mechanism of Creep in Metals. W. A. Wood and H. J. Tapsell. (Nature, 1946, vol. 158, Sept. 21, pp. 417–418). When a single metal crystal is loaded, a dislocation of the mosaic structure occurs, but the mosaic elements in general remain approximately parallel. This condition is called the “parallel crystallite formation,” to distinguish it from the case of the polycrystalline metal. This difference in the fundamental process of breakdown might be a factor distinguishing the normal short-time deformation of a polycrystalline metal in a tensile test with increasing stress from continuous deformation at the much slower rate known as creep. An experiment with aluminium is described which proves that such is actually the case.

Graphite in Cast Iron. A. W. Silvester. (Australian Institute of Metals: Australasian Engineer, 1946, July 8, pp. 82–90). The effects of the total carbon content, silicon, nickel, and copper on the distribution and form of the graphite in cast iron are dealt with in detail in the first part of this paper, whilst factors affecting the form and distribution of the graphite, and the influence of this distribution on the mechanical properties of cast iron, are discussed in the second part.

Special Cast Irons. K. H. Sutcliffe. (Australian Institute of Metals: Australasian Engineer, 1946, Aug. 6, pp. 37-43). The composition and properties of special cast irons are discussed under the following headings: (a) Straight nickel irons; (b) straight chromium irons; (c) straight copper irons; (d) effects of combinations of alloying elements; (e) effects of molybdenum and vanadium in conjunction with other elements; (f) high-silicon irons; and (g) inoculated irons.

Some Notes on Hard Wear-Resisting Cast Irons and Steels. M. Ballay and R. Chavy. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 80, Sept. 19, pp. 55-61). The compositions and properties of a number of wear-resisting cast irons and cast steels developed at a French foundry are reviewed. These include: (1) An iron with a sorbitic structure as-cast, requiring no heat-treatment; (2) an iron machinable as-cast for subsequent quenching and tempering; (3) a martensitic iron for aero-engine cylinders, requiring heat-treatment before machining; (4) a nickel-chromium cast iron for wire-drawing drums; (5) white sand-cast irons; (6) grey chill-cast irons; and (7) three nickel-chromium oil-hardening crucible cast steels.

Some Investigations of 18-8 Stainless Steel. W. G. Hubbell. (Steel Processing, 1946, vol. 32, July, pp. 455-459). Investigations of the pressing and forming characteristics of chromium-nickel stainless steels are described. The conclusions reached were: (1) The forming properties improve as the amount of free ferrite decreases; (2) the amount of free ferrite is inversely proportional to the nickel content; (3) increasing the nickel content from 8% to 11% improves the forming properties; (4) "dead soft" 18/8 stainless steel reaches the breaking point more quickly than 18/10 steel; (5) "dead soft" 18/8 steel tends to wrinkle in one place rather than over a wide area; and (6) titanium-stabilized stainless steel has greater ductility than the columbium-stabilized type.

Corrosion and Heat Resisting Steels. A. M. Bennett. (Australian Institute of Metals: Australasian Engineer, 1946, Aug. 6, pp. 66-69). The mechanical, electrical, heat-resisting, and corrosion-resisting properties of ferritic, martensitic, and austenitic stainless steels are discussed. Strongly oxidizing acids such as nitric acid do not damage stainless steels under a wide variety of conditions, but strongly reducing acids, notably hydrochloric acid, cause rapid attack. Sulphuric acid is a borderline case; small additions of other salts frequently render this acid quite innocuous.

Triple Alloy Structural Tubing. C. M. Schwitter. (Iron Age, 1946, vol. 158, Aug. 22, pp. 46-49). Details are given of the physical properties and weldability of tubes of steel 8630. This is a low-alloy steel containing chromium 0.40-0.60%, nickel 0.40-0.70%, and molybdenum 0.15-0.25%. It has a very high strength/weight ratio and is used for tubes for mounting aero-engines.

Gas Turbines. C. C. Hall. (Iron and Steel, 1946, vol. 19, Aug., pp. 455-457; Sept., pp. 499-501, 505). The metallurgical problems involved in the materials for the modern gas turbine are indicated and data

are presented on the properties of steels used in its construction.

Selection of Die Steels for Cold Working Metals. G. M. Butler. (American Society of Tool Engineers: Steel, 1946, vol. 119, Aug. 19, pp. 124-127). The properties of water-, oil-, and air-hardening die steels and their selection for various applications are discussed. Tables are presented classifying a number of alloy die steels in order of decreasing distortion, toughness, wear-resistance, and machinability.

Die Steels for Hot Work. D. W. Rudorff. (Metallurgia, 1946, vol. 34, Aug., pp. 189-193). German and Russian investigations on the development of substitutes for the high-tungsten tool steels are reported. The data are taken from a paper by R. Hohage, W. Völker, and R. von Tinti (*see* Journ. I. and S.I., 1945, No. I., p. 61 A), and a Russian paper by J. A. Heller and A. Y. Truskov. The Russian authors found that a tool steel can be given the required mechanical strength by adding 1-1.5% of chromium, whilst the required high critical temperature can be obtained with a silicon content of 1.0-1.5%. The carbon content should be kept at 0.3-0.4%. The Russian efforts towards dispensing with tungsten have been mainly directed towards silicon-manganese-chromium steels.

Steels for Die Casting Die Blocks. J. L. Erickson. (Materials and Methods, 1946, vol. 24, Aug., pp. 389-396). The requirements of steels used for the dies for die-casting non-ferrous metals and alloys are discussed, and particulars are given of the composition and properties of many steels for this purpose; these are grouped under the general headings: (1) Steels for lead and tin base alloys; (2) steels for zinc base alloys; (3) steels for aluminium and magnesium base alloys; and (4) steels for copper base alloys.

Calculation of Stress in Crane Hooks. A. M. Wahl. (Journal of Applied Mechanics, 1946, vol. 13, Sept., pp. A-239-A-242). Two methods for calculating stress in crane hooks, which have given good results in practice, are described.

On the Stresses in Hooks, and Their Determination by Relaxation Methods. L. Fox and R. V. Southwell. (Proceedings of the Institution of Mechanical Engineers, 1946, vol. 155, pp. 1-6). The "semi-inverse" method of Saint Venant has been applied to hooks by Golovin in 1881 and by Southwell in 1942. The actual hook is replaced in calculation by a half-tore (a moulding of semi-circular profile) sustaining shear stresses appropriately distributed over its terminal sections, and having a cross-section identical with the principal section of the hook. Southwell's solution is a formal one applicable to any shape of section; it involves two stress-functions related by three conditions at the boundary. In the present paper, stress distributions are determined on the basis of Southwell's solution for two British Standard hooks, the first of trapezoidal and the second of circular cross-section.

Aeronautics and the Metallurgist. L. Aitchison. (Journal of the Royal Aeronautical Society, 1946, vol. 50, Sept., pp. 677-693). The improvements which have taken place since 1914 in the properties of metals and alloys used in aeroplane construction

are reviewed. Studies of the behaviour of metals in the physico-chemical sense have led to the mathematical treatment of the behaviour of the metal crystal itself; this and the directionality of properties relative to the crystal axes are discussed and it is suggested that efforts should be concentrated on improving manufacturing technique.

Substitute Metallurgical Products. A. M. Portevin. (Metal Progress, 1946, vol. 50, Sept., pp. 485-494). The availability in France of the materials for making alloy steels and non-ferrous alloys at the beginning of the war and during the German occupation, and the development of substitute materials and their properties are reviewed.

German Metallurgical Laboratories for Ferrous Metals with Special Reference to the K.W. Institute for Iron Research. (British Intelligence Objectives

Sub-Committee, 1946, Final Report No. 676: H.M. Stationery Office). Visits to German metallurgical laboratories are reported, the object being to study the work, equipment, and methods used. The principal part of the report deals with the organization, work, and equipment at the Kaiser-Wilhelm-Institut für Eisenforschung, but short accounts are also given of the laboratories at Bergakademie Clausthal-Zellerfeld, Göttingen University, the Wöhler Institut, the technical colleges in Hanover and Aachen, August Engels G.m.b.H., Wirtschaftsgruppe Eisengiessereien, the Deutsche Eisenwerke, and Kurbenwellenwerke G.m.b.H.

Acid Resisting Silicon Iron Pipes and Pipe Fittings (Elbows, Bends, Tees, Crosses). (British Standards Institution: British Standard No. 1333, 1946).

METALLOGRAPHY AND CONSTITUTION

(Continued from pp. 100 A-101 A)

The Electron Microscope and Its Application to the Study of Metals. R. G. Picard. (Metallurgia, 1946, vol. 34, Aug., pp. 181-185). The principles of the electron microscope are explained and its application to the study of metals is described. The electron microscope has a depth of focus that is great compared with that of the light microscope; this makes possible the production of stereoscopic micrographs. A scanning electron microscope has been constructed, but its development was halted temporarily by the war.

A Study of Distortion in Electron Microscope Projection Lenses. J. Hillier. (Electron Microscope Society: Journal of Applied Physics, 1946, vol. 17, June, pp. 411-419). It is shown that: (1) Relatively small amounts of distortion in the projection lenses of electron microscopes can produce serious disturbances in particle size distributions obtained with the instrument; and (2) it is both theoretically and practically possible to design a projection lens system for an electron microscope in which, at least at one magnification, the distortion due to spherical aberration of that lens is reduced to negligible proportions.

Nondestructive Measurement of Residual and Enforced Stresses by Means of X-Ray Diffraction. I. G. Sachs, C. S. Smith, J. D. Lubahn, G. E. Davis, and L. J. Ebert. (National Advisory Committee for Aeronautics: Welding Journal, 1946, vol. 25, July, pp. 400-S-412-S). The X-ray diffraction method of measuring enforced and residual stresses in metal is not sufficiently developed for commercial application. An attempt is made to clarify the present situation by studying the literature and evaluating the available techniques. The bibliography contains 73 references.

Industrial X-Ray Field in Germany. (British Intelligence Objectives Sub-Committee, 1946, F.I.A.T. Final Report No. 535: H.M. Stationery Office). A brief review of the types of X-ray equipment available for industrial purposes in Germany is presented together with a bibliography of German literature

on non-destructive methods of testing published during the period 1940-45.

Industrial Radiology. R. H. Cooke. (British Engineering Export Journal, 1946, vol. 29, Sept., pp. 337-345). The production of X-rays, their properties, and how they are controlled and interpreted are explained and illustrated descriptions are given of X-ray equipment of different capacities and their industrial applications.

Determination of Grain Size in Mild Steels. B. D. Enlund and G. Sehlberg. (Jernkontorets Annaler, 1946, vol. 130, No. 8, pp. 273-284). (In Swedish). The JKM grain-size chart which was introduced in 1937 (see Journ. I. and S.I., 1938, No. I, p. 157 A) was prepared by making a tracing of an actual micrograph and reproducing this at different magnifications. In recent work involving the examination of a large number of steels a series was taken out which represented one each of the JKM scale numbers 6 to 13 inclusive. Their grain sizes were from 64 to 8192 sq. μ ., and covered the range of commercial mild steels. These were etched, and macrographs and micrographs at 5 and 100 diameters respectively are presented in a series of plates so that the grain size of a mild steel can readily be determined by comparison. The JKM grain size can be converted into the A.S.T.M. grain size by subtracting the JKM number from 16.

The Sigma Phase. F. B. Foley. (Alloy Casting Bulletin, 1945, July, pp. 1-9). Investigations on the crystallographic form and characteristics of the hard brittle non-magnetic compound known as the sigma phase are reviewed. At first identified as the simple compound FeCr, it has been found that its composition may be extended to take in other elements without affecting its crystallographic form. The phase is stable below about 1700° F., but at higher temperatures it transforms to ferrite. This transformation is a sluggish one. Etching and magnetic methods of detecting this phase are described.

ORES—MINING AND TREATMENT

(Continued from p. 85 A)

Raw Materials. (Steel, 1946, vol. 119, Sept. 23, Supplement). Data on shipments of Lake Superior ores during the last 85 years are presented and discussed. The benefits obtained by cleaning coking coals are also reported.

The Mode of Occurrence of Manganese in Silicate Ore from Basttjärn and Chemical-Metallurgical Leaching Tests. H. Löfquist. (Teknisk Tidskrift, 1946, vol. 76, Sept. 14, pp. 885-893). (In Swedish). One of Sweden's most northerly iron ore beds, the Basttjärn field, contains some 14 million tons of skarn-rich ore with more than 1% of manganese. As a high proportion of this manganese is lost in the ordinary iron- and steel-making processes, methods of recovering more manganese in a form suitable for steelmaking have been investigated. This paper discusses the form in which the manganese is present in the ore and the distribution of the manganese, iron and silica in the different grain sizes on crushing. Tests of methods of obtaining a concentrate richer in manganese, by magnetic separation, magnetizing-roasting, oxidizing-roasting, followed by the Bradley process, and leaching with hydrochloric acid are described.

The Latest Developments in Electrostatic Concentration. A. A. Linari-Linholm. (Teknisk Tidskrift, 1945, vol. 75, Nov. 10, pp. 1229-1236). (In Swedish). Electrostatic separation is a method of separating fine-grained materials by means of a high-tension field. The conditions for successful separation are that the two materials are different physically and that there is a marked difference in their electro-physical properties. The history of electrostatic separation is reviewed and the theory is explained, and descriptions are given of the principal features of separators designed by (a) Blake and Morscher, (b) Huff, (c) H. B. Johnson, (d) F. Fraas and O. C. Ralston, (e) H. L. Bullock, (f) H. M. Sutton and G. W. Jarman, jun., and (g) United States Bureau of Mines. Examples of the application of the process in a variety of industries in America and Germany and data on the capital outlay and operating costs are quoted from the literature. It is not expected that electro-

static separation will replace flotation, magnetic, or wet mechanical methods, but it can be used in combination with these to improve the efficiency.

Rationalization in Swedish Iron-Ore Dressing. S. Mörtzell. (Jernkontorets Annaler, 1946, vol. 146, No. 9, pp. 369-460). (In Swedish). After a short review of recent developments in the machinery at Swedish iron-ore dressing plants, some problems of current interest in connection with ore dressing are discussed. The results of a series of ball-mill grinding tests are given; these illustrate the effect of ball size on the grinding as well as on the quality of the product. The blastfurnaceman's desire to have a concentrate which is higher in iron and at the same time coarser in grain has led to the problem of locked particles of magnetite ores, and this has caused extensive studies to be made of the liberation properties in the comminution of different ores. These studies included systematically arranged and evaluated elutriation analyses which have proved to be valuable when a basis is required for estimating the feasibility of obtaining rich and coarse-grained concentrates. Examples are cited of ore dressing by combining concentration with jigs or shaking tables with magnetic concentration. It has been found that the phosphorus content of certain ores could be considerably reduced by extended concentration. Experiments in leaching with acids are reported. Flotation of the pyrrhotite at a very low pH value has given good results for eliminating pyrrhotite from certain iron ores.

After a discussion of the supervision and control of ore-dressing plants and the principles to be observed in the planning of such plants, data on several Swedish installations are given. A comparison of the data is made, and this demonstrates the measures taken in recent years to achieve rationalization.

New Metallurgical Experience with Sintering. B. Hessle. (Iron and Steel Institute, 1946, Translation Series No. 289). This is an English translation of a paper which appeared in Jernkontorets Annaler, 1945, vol. 129, No. 8, pp. 383-446. (See Journ. I. and S.I., 1945, No. II., p. 175 A).

REFRACTORY MATERIALS

(Continued from pp. 104 A-108 A)

The Development of Monolithic Dolomite Linings. The Technical Panel of the Basic Furnace Linings Committee. (Iron and Steel Institute, 1946, Special Report No. 33). The work described in this Report constitutes the outcome of a co-operative effort carried out by a number of interested firms who agreed to pool their knowledge and carry out joint research into the problem of monolithic dolomite linings for steel furnaces. Owing to the difficulty of importing the magnesite and chrome ore during the war years, it became a matter of national importance

to intensify the search for alternative methods of lining furnaces. A Technical Panel was set up, and by the end of October, 1940, the stage had been reached when large-scale practical trials with a dolomite prepared from indigenous materials could be made, and the special case of open-hearth furnaces could be investigated in detail. In all, over a hundred technical reports have been communicated to the Panel.

The Report was first issued confidentially by the Institute, and was discussed at a private meeting

at York on September 12th, 1941, and at Leeds on November 6th, 1941. Contributions to the discussions and the authors' replies are included at the end of the Report. The need for secrecy no longer exists, and the Report is now published. It consists of six Sections, abstracts of which follow.

The Properties of Dolomite and the Manufacture and Testing of "Basic." A. L. Bradley, J. H. Chesters, and M. Douglas. (Iron and Steel Institute, 1946, Special Report No. 33, Section I.). The raw material for the manufacture of burned dolomite, called "basic" in the trade, is a true dolomite ($\text{CaMg}(\text{CO}_3)_2$) with a low flux content and a variable porosity. Laboratory firing tests show that this material breaks down rapidly above 700° C. with a large increase in porosity, and on reaching 1200° C. begins to shrink. The specific gravity of the product bears little relation to the firing treatment, but the porosity decreases, being as low as 2% with extremely hard fired material. A more typical figure is 10–15% with a bulk density of 2.70 g. per ml.

The rate of hydration both in the atmosphere and in steam increases with the fineness of grinding and decreases as the firing temperature is raised. The hydration is accompanied by crumbling, frequently referred to as "perishing." Packing-density experiments show that a dense aggregate can be produced by using the optimum-packing-density mixtures in various ternary, quaternary, and quinary systems. Even so, the values obtained by sieving-out and remixing, using up to seven grain-size groups, are lower than those obtainable by controlled grinding in a pan mill. The sintering of basic is shown to be a function of the quantity of fine material present. Permanent stabilization can be obtained by the addition of various oxides prior to kiln-firing, while temporary stability can be given to basic by the use of suitable oils or by grinding with stearic acid.

An Addendum to this Section, by A. L. Bradley and A. H. Jay, records a study of the atomic structure of dolomite and the structural changes produced during heating. Recourse has been had to loss-in-weight measurements and X-ray analysis. The breakdown of dolomite is shown to begin at about 600–650° C. and to be completed at about 900° C. A large proportion of the dolomite decomposes, giving magnesia, before the calcium carbonate present breaks up into lime and carbon dioxide. The crystal size of the magnesia and lime formed from the purer dolomite is remarkably fine, even after firing to 1780° C. Impurities play a part in crystal development, so that crystal size is not regarded as any indication of firing treatment.

The Processing of "Basic" for Use in Furnace Linings. A. H. B. Cross, D. F. Marshall, and R. J. Sarjant. (Iron and Steel Institute, 1946, Special Report No. 33, Section II.). This paper reviews the present state of knowledge in regard to the preparation of basic in a form suitable for furnace linings.

The dry grinding of lump basic in perforated-bottom pan mills and the final dry grinding in solid-bottom pan mills are discussed in detail. The major factors governing the dry grinding of basic in solid-bottom pan mills appear to be :

- (i) The size and type of the mill employed.
- (ii) The mechanical properties of the dolomite.

These have been investigated and an attempt has been made to correlate all available pan-mill data and develop a general mathematical formula governing the breakdown of basic. This breakdown is of an exponential character. The high packing density of the milled product is due to a selective crushing of the softer particles of lower bulk density and to a rounding of the larger particles. A study has been made of the mixing of dry dolomite and tar and its bearing on the preparation and use of a mixture suitable for ramming furnace linings. A review is given of the characteristics of the machinery suitable for the preparation of basic.

The Electric Arc Furnace. A. H. B. Cross and T. R. Walker. (Iron and Steel Institute, 1946, Special Report No. 33, Section III.). Following initial experiments to determine how a lining of specially graded basic with a high packing density would behave in contact with molten steel, both in the dry and in the tar-bonded condition, the new type of lining was installed in a number of steel-making arc furnaces engaged in regular production work. These furnaces were of various designs and their capacity ranged from 2 to 30 tons. The graded basic is effective, whether used dry or bonded with dehydrated tar, but from a practical point of view it is much easier to install a lining with the tarred basic, especially on the sloping parts. Dry graded basic such as is used for the hearth is not very suitable for fettling between heats, as it does not leave the shovel cleanly and spreads too much. Further experimental work is necessary before definite recommendations can be made regarding the type of basic likely to give the best results for this purpose. This work is now in progress.

Application of Dolomite Linings in Open-Hearth Furnaces. J. C. Hayman, D. F. Marshall, and E. Shaw. (Iron and Steel Institute, 1946, Special Report No. 33, Section IV.). This paper describes a technique which has been evolved to produce a more durable bottom for the basic open-hearth furnace. A fundamental principle of the methods adopted is the reduction of the intergranular porosity of the rammed material by grinding in solid-bottom pan mills for a specified time. The preparation of the material and the technique of ramming are discussed in detail, and the methods of bringing the rammed hearths into operation are compared. A summary of the practical methods of hearth installation at various plants is given.

The Basic Open-Hearth Furnace. A. L. Bradley, J. H. Chesters, J. M. Ferguson, and R. J. Sarjant. (Iron and Steel Institute, 1946, Special Report No. 33, Section V.). A description is given of the technique employed in Great Britain for the installation of open-hearth furnace bottoms. It is found that stabilized dolomite bricks can be used quite safely in the sub-hearth and that much improved results can be obtained in the monolithic section by controlling the grinding and tarring of the calcined dolomite ("basic") so as to obtain the optimum packing density. The intergranular porosity of new hearths

made in this way is about 12%, as compared with about 35% for the old type. The greater packing density results in a marked increase in durability, which shows itself in reduced fettling time and dolomite consumption and most markedly in an unusually long trouble-free period at the start of the campaign.

The maintenance of hearths, *i.e.*, drainage and fettling, is still the major problem, but the work in this field is at too early a stage to warrant the making of definite recommendations.

Experiments on hot-metal furnaces suggest that the main difference between hard and soft bottoms lies in the decreased basicity of the latter.

Microscopic examination of used hearths shows that the main attack is due to the entry into the hearth of slags rich in iron oxide and lime. The iron oxide presumably comes from the oxidation of metal left on or in the hearth, whilst the lime comes from the lime charged. The hearth is also attacked by silica, presumably from the silicon in the pig iron and to a less extent from the silica refractories, by phosphorus and by alumina of uncertain origin. The magnesia in the basic absorbs FeO and MnO in solid solution, but otherwise remains essentially inert. The lime, on the other hand, combines with the silica to form tricalcium silicate and with the iron oxide and alumina to form solid solutions of the brownmillerite ($4\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$)/dicalcium-ferrite ($2\text{CaO} \cdot \text{Fe}_2\text{O}_3$) type. The $3\text{CaO} \cdot \text{SiO}_2$ is quite refractory, but the solid solutions are very fluid at the working temperature and penetrate deeply into the hearth or back wall.

There is little doubt that the surface layers play a part in the bath reactions due to the alternate oxidation and reduction of the iron oxide, but the extent of the reaction is uncertain, and since such reactions generally increase the wear on refractories, a denser and less reactive hearth is considered essential.

Preliminary trials of graded basic in back-wall panels have given encouraging results. The conditions are oxidizing and consequently the iron oxide does not go into solid solution in the lime and magnesia as in the hearth, but rather reacts with them to form magnesio-ferrite, dicalcium ferrite, and brownmillerite. The attack by siliceous drip from the roof can be minimized by using a course of chrome or chrome-magnesite bricks at the top of the wall.

The Preparation and Utilisation of Dolomite at the Corby Works of Messrs. Stewarts and Lloyds, Ltd. W. C. Bell. (Iron and Steel Institute, 1946, Special Report No. 33, Section VI.). This paper gives the analyses, method of preparation and grading characteristics of the materials used in maintaining the dolomite linings of a steel plant producing half a million ingot tons of steel per annum. A detailed description of the dolomite plant is given, including plant layout and notes on the crushers and mills used in the preparation of the tarred dolomite mixture intended for lining both the converters and the electric furnace. The machine for producing rammed converter bottoms, as separate units, and the ovens for firing these are described, the whole being illustrated by diagrams. The method of ramming bottoms and linings for the converters and for both hearth and walls of the electric furnace is given in detail. The practice developed for

burning-in and slagging both converter and electric furnace linings is detailed, as is the method of firing the bottoms, with notes on the importance of control at this stage. The importance of control over the tar content of the mixture intended for use under different conditions is also stressed.

Details of the life of the electric-furnace bottom and walls are given, together with the fettling experience. Notes on the use of dolomite and tarred-dolomite mixture for other purposes than those given above are included. Finally, the influence of various factors, notably the silicon content of the iron used, on the life of dolomite linings is discussed in the terms of the detailed investigation carried out on converter bottoms.

Second Report on the Development of Monolithic Dolomite Linings. The Technical Panel of the Basic Furnace Linings Committee. (Iron and Steel Institute, 1946, Special Report No. 35). Since the first report of the Technical Panel of the Basic Furnace Linings Committee was presented at the York Meeting in 1941, further work has been carried out on the development of monolithic dolomite linings for furnaces. Research has been directed principally to improving the fettling of furnace linings.

At the York Meeting the Committee's use of the term "basic" was the subject of some criticism, and it has since been agreed to substitute the term "doloma," and this is therefore used throughout the present report.

It has been fairly well established that the life of a furnace bottom, in so far as it may be influenced by the character of the materials used and the initial ramming, is improved by adherence to the recommendations laid down in the First Report.

The above information is set out in the introduction by M. Douglas and R. J. Sarjant, which also contains lists of members of the Basic Furnace Linings Committee and of the Technical Panel of the Committee. The Report is in five Sections. Section I. is on the properties of fettling materials, and the remaining four Sections deal respectively with fettling and the use of doloma in open-hearth furnaces, electric-arc furnaces, basic Bessemer converters, and mixer ladles. Abstracts of the papers follow.

The Properties of Fettling Materials. A. L. Bradley, J. H. Chesters, and D. F. Marshall. (Iron and Steel Institute, 1946, Special Report No. 35, Section I., pp. 9-27). The quality of doloma may be expressed in terms of bulk density, chemical analysis (including the loss-on-ignition of the through-72-mesh fraction), and grading. Quality control is applicable to the lump or the ground material, but the bulk density of a coarse fraction from lump doloma will be less than that of ground doloma of similar origin, owing to selective grinding. Crushed doloma deteriorates more rapidly than lump doloma, but either material may be stored in sealed containers for a period of at least six months. Under such conditions tarred graded material tends to lose its ramming properties, but these may be restored to a large extent by reheating and mixing with 2% of creosote. It is preferable to store dry graded doloma and make any

tar addition immediately before use. The influence of grading on packing density is less for thrown material, but the permeability tends to vary inversely with the packing density. The addition of small amounts of tar increases the permissible amount of fines for a given permeability. The "dynamic" angle of repose bears little relation to the "static" angle when graded doloma is thrown. Addition of tar increases the angle of repose of fine gradings. The thermal conductivity of fine unsintered doloma is low, resulting in a very thin sintered zone in a furnace wall. Of the material examined, iron oxide and stabilized dolomite appear to be most useful in promoting sintering.

The Properties of Fettingling Materials. Addendum I. The Tar Bonding of Doloma. W. L. Kerlie. (Iron and Steel Institute, 1946, Special Report No. 35, Section I., pp. 27-49). An apparatus developed for the routine testing of tarred doloma has been utilized for research work on the influence of tar on the characteristics of the material. The existence of an optimum tar content has been established, above and below which the properties of the rammed material are impaired. The effects of the naphthalene content and the viscosity of the tar have been given consideration.

From the information obtained on the expansion of tarred doloma during heating-up, suggestions are made for improving furnace linings and avoiding some of the troubles that have been experienced; information is also given on the influence of certain factors on the rate of hydration. The properties of tars used in various steelworks have been examined and the effect of exposure on samples rammed with those tars noted. Data are given relative to the influence of tar on the cold crushing strength and stability in storage of rammed doloma after firing at different temperatures.

The Properties of Fettingling Materials. Addendum II. Correlation of Pan-Mill Data. D. F. Marshall. (Iron and Steel Institute, Special Report No. 35, Section I., pp. 49-54). Further studies of the grinding characteristics of a total of 11 pan mills have confirmed the original indications that the production of the various size fractions follows an exponential law. The two major factors governing the grinding of doloma in pan mills appear to be (a) the total crushing load and (b) the weight of doloma charged.

A satisfactory correlation of data from various mills has been obtained, indicating that the optimum crushing load lies between 8 and 9 tons. Beyond this point no material benefit is obtained by increasing the crushing load unless wider rolls are used; this course is not recommended, as it usually results in increased maintenance charges. The second important variable in the rate of grinding has been shown to be the weight of material charged to the pan, the optimum grinding time varying almost linearly with the weight of doloma charged. The correlation obtained offers a satisfactory basis for the choice of new equipment.

The Fettingling of Open-Hearth Furnaces. J. H. Chesters, F. L. Robertson, and E. Shaw. (Iron and

Steel Institute, 1946, Special Report No. 35, Section II., pp. 54-70). It is suggested that the following factors tend towards high doloma consumption and long fettling time: (1) Inadequate ramming of the hearth, (2) over-insulation of the hearth, (3) the use of cold-pig fixed furnaces rather than the hot-metal tilting type, (4) the production of low-carbon steels requiring slags high in iron oxide, (5) the age of the hearth, (6) the use of soft-fired doloma, and (7) exceedingly coarse or fine gradings. With regard to item (7), tarred Committee-type gradings as used for bottoming, either alone or mixed with normal fettling material, were found to give good results.

The relative efficiency of different grades of fettling can be determined only in conjunction with detailed records dealing with the bottoms concerned. Trials on a single furnace which is behaving consistently and in which the normal fettling material is used both before and after the test period are recommended. Local deterioration of the hearth increases with age and should be dealt with by cutting out the affected area and re-ramming. After a limited period—usually two to three years—the complete renewal of the hearth may prove more economical, in view of the lower fettling time and the reduced consumption of fettling material consequent upon the installation of a new hearth and the relative freedom from long fettling periods. Local failures may be due to inadequate fettling or to special metallurgical conditions, *e.g.*, the use of high-silicon scrap.

The Fettingling of Open-Hearth Furnaces. Addendum I. Miscellaneous Factors Affecting Hearth Life. J. H. Chesters, F. L. Robertson, and E. Shaw. (Iron and Steel Institute, 1946, Special Report No. 35, Section II., pp. 71-75). Laboratory tests on small doloma crucibles suggest that the iron oxide formed by oxidation of the metal is far more corrosive than basic slag. It is therefore concluded that it is better to "slag" a bottom previous to use than to allow metal to get into open pores. Over-insulation of a doloma hearth has been shown to lead to softness of the surface and a consequent increase both in fettling consumption and fettling time.

The Fettingling of Open-Hearth Furnaces. Addendum II. Monolithic Doloma Doors and Wing Walls. R. C. Baker. (Iron and Steel Institute, 1946, Special Report No. 35, Section II., pp. 75-79). Rammed tarred Committee doloma has successfully been applied to open-hearth furnace doors suitably studded with 1-in. steel pegs and giving lives approximately double that of firebrick. The main difficulty and chief cause of wear is flaking of the working face. Useful results have also been obtained in wing walls.

The Fettingling of Open-Hearth Furnaces. Addendum III. Tap-Hole Construction and Maintenance. E. Shaw. (Iron and Steel Institute, 1946, Special Report No. 35, Section II., pp. 79-82). Tap-hole maintenance can be reduced by lining with stabilized dolomite and using cement patching to maintain the contour, thus eliminating the necessity for piping tap-holes. Results prove that such tap-holes have longer lives in furnaces making low-carbon steels.

The Fettling of Open-Hearth Furnaces. Addendum IV. An Analysis of Factors Affecting the Consumption of Doloma in Open-Hearth Furnaces. A. Brown and D. H. Ward. (Iron and Steel Institute, 1946, Special Report No. 35, Section II., pp. 82-97). The data examined concerned furnaces at three different works—two at Shotton and one at Shelton. The principal aim of the investigation was to assess the importance of the factors affecting fettling time and doloma consumption, with a view to decreasing either or both.

The first records to be considered were those of *T* furnace, Shotton, giving details of 15 factors for each cast. The main factors affecting fettling time were sorted out and studied more closely. Two factors were important—the boiling time and the age of the bottom. The fettling time increased by 10 min., on the average, for every 100 casts, and by 24 min., on the average, for an increase of 1 hr. in the boiling time. Equally important was the evidence that some factors (including the ferrous oxide content of the slag) did not affect the fettling time to any marked degree. Records of doloma consumption for individual casts were not available, but a check was obtained from the weekly bottom summaries for the particular furnace, showing that doloma consumption and fettling time increased simultaneously.

The second group of data gave the bottom-record summary for 13 furnaces over a similar period of time, giving average values of several factors for sets of 50 consecutive casts. They showed an increase of fettling time with the age of bottom, varying between 3 and 14 min. per 100 casts. The other prominent effect was that the fettling time decreased as skulls weighing over 5 cwt. became more frequent, *i.e.*, as the tapping temperature decreased. This suggests that a balance needs to be struck between the temperature and the boiling time (the importance of which is shown by the first group of data). Unfortunately the boiling times were not recorded in sufficient detail for them to be used in the analysis of groups of furnaces.

The third group of data gave detailed records for seven separate furnaces. The factors found to be of most importance were boiling time, ingot output, and age of bottom. These factors are considered separately for each furnace, and finally proposals are made for the introduction of control charts on doloma consumption and boiling time.

None of the factors examined can be given as the sole cause of the variations in fettling time from 30 min. to 2 hr. This appears to be fundamental to the process as it is carried out at present. One factor—

excessive boiling time—has been isolated, however, as liable to give long fettling times.

The Fettling of Open-Hearth Furnaces. Addendum V. The Development of a Simple Repair Technique for Holes in Doloma Hearths. E. Shaw. (Iron and Steel Institute, 1946, Special Report No. 35, Section II., pp. 98-101). The difficulties normally experienced in repairing holes in furnace bottoms can be overcome by dropping into the hole a bag of stabilized dolomite. This not only provides a dense and readily sintered patch but also splashes out most of the metal present in the hole. Such patches are preferably covered with a 2-in. layer of doloma which is burned on to give a final working surface. Even better results were subsequently obtained by bonding pea-sized stabilized dolomite clinker with stabilized dolomite cement.

Doloma Linings and Fettling Materials in Electric-Arc Furnaces. W. L. Kerlie, R. J. Sarjant, and T. R. Walker. (Iron and Steel Institute, 1946, Special Report No. 35, Section III., pp. 101-127). The technique employed in the preparation, ramming, and putting into service of both dry and tarred doloma for the hearths of electric-arc furnaces is described. The grading of fettling material, methods of application, and the factors affecting fettling consumption and bottom life are discussed. A standard lining technique applicable to the installation of monolithic doloma side walls is outlined, together with the results of chemical, mineralogical, and X-ray examination of the changes in the monolith during service.

The Application of Doloma in Basic Bessemer Converters. W. L. Kerlie. (Iron and Steel Institute, 1946, Special Report No. 35, Section IV., pp. 127-136). The effects of stabilized dolomite, hard-burned doloma, and additions of scale, bauxite, and coke to the normal soft-fired doloma have been investigated and the influence of varying percentages of doloma recovered from old linings on the performance of converter bottoms has been considered. Notes are included on the effect of milling time, manganese and silicon content of the iron, iron temperature, the conditions of firing the lining of the converter, and the tar content of the tarred doloma.

The Utilization of Doloma in Mixer Ladles. W. L. Kerlie. (Iron and Steel Institute, 1946, Special Report No. 35, Section V., pp. 136-140). A description is given of the relining methods adopted and the results obtained during service on three 25-ton mixer ladles, of which one was lined with stabilized dolomite brick and the other two with tarred doloma rammed behind a retaining wall of (a) firebrick and (b) stabilized dolomite brick.

FUEL

(Continued from pp. 108 A-109 A)

Combustion Tests on South African Anthracite and Coal. F. W. Quass. (Journal of the Chemical, Metallurgical and Mining Society of South Africa, 1946, vol. 47, July, pp. 1-47). A description is given of tests designed to establish the relative suitability for steam-raising purposes of South African anthracite. A number of nut-size coals and anthracite were used in an experimental furnace, fired by hand. The anthracite compared favourably with normal industrial coals under forced-draught conditions, 1946—ii

ability for steam-raising purposes of South African anthracite. A number of nut-size coals and anthracite were used in an experimental furnace, fired by hand. The anthracite compared favourably with normal industrial coals under forced-draught conditions, K

where medium to low steaming rates are required. With natural draught its performance is only equal to that of low-grade coals.

Smoke Abatement. D. J. Bradbury. (Iron and Steel, 1946, vol. 19, Nov., pp. 598-600). The present position in relation to the laws concerning smoke abatement is discussed. The author gives hints on how to avoid the waste of fuel in smoke, and advocates a more considered approach to the problem of smoke prevention.

Coal as a Fuel for the Gas Turbine. J. I. Yellott. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 2086: Coal Technology, 1946, vol. 1, Aug.). A review is made of the fuel resources of the United States, which shows that while the reserves of oil and natural gas will be exhausted in the next thirty years, the supply of coal is practically unlimited. Atomic energy is not likely to be economically available for many years to come, and it is therefore necessary to consider how coal may be utilized more effectively. The author describes the use of an open-cycle gas turbine which is

suitable for use in locomotives. The costs of a locomotive with such a turbine should be far less than those of the diesel-electric types now in use, because of the lower fuel consumption and the reduced man-power requirements. The problems to be solved in applying a solid fuel to a gas turbine are: (1) Preparation of the fuel; (2) combustion within a limited space; and (3) the removal of the fly-ash to the extent required for adequate life of the turbine blades. These are discussed in relation to a suggested coal-burning turbine and diagrams are given of mechanisms designed to overcome them.

Grinding of Anthracite for Pulverized Fuel. C. H. Frick. (American Institute of Mining and Metallurgical Engineers, Technical Publication 2061: Coal Technology, 1946, vol. 1, Aug.). A short account is given of the history of anthracite as a fuel. The plants at Pine Grove and Hauto, Pennsylvania, using pulverized anthracite are described. The main features of the preparation of the fuel are the drying, by means of hot gases, and the crushing, in horizontal ball mills.

PRODUCTION OF IRON

(Continued from p. 109 A)

Blast Furnaces—Notes on German Practice. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 819: H.M. Stationery Office). An account is given of visits to eight German blast-furnace plants and to a works manufacturing carbon paste and carbon bricks for lining blast-furnaces.

Maintenance of the Blast Furnace Cooling Systems. G. Calder Little. (Iron and Steel Engineer, 1946, vol. 23, Sept., pp. 112-113). A method employed by the Bethlehem Steel Company to clean the 1½-in. pipe connecting blast-furnace cooling blocks is described. The solution used was 10% hydrochloric acid containing an inhibitor. One set of blocks was filled at a time. After acid appeared at the discharge, the supply valve was closed and the temperature of the blocks was allowed to rise to 170° F. when water was turned on to flush out the acid. This process was repeated until a desirable rate of flow was obtained.

Effect of Sized and Nodulized Mesabi Iron Ores on Blast Furnace Performance. H. F. Dobscha. (American Iron and Steel Institute: Blast Furnace and Steel Plant, 1946, vol. 34, Aug., pp. 979-985). A detailed account is given of full-scale tests on the effects of ore preparation on blast-furnace performance. The tests were carried out on two identical 27 ft. 6 in.-hearth furnaces at the Edgar Thomson Works of the Carnegie-Illinois Steel Corporation, a mixture of beneficiated Mesabi ores being charged on one furnace for a continuous two-month period, while normal ores of the same groupings were charged on the other furnace. During an interim period of one month the burdens were reversed, and the tests were con-

tinued for another two-month period. Except for minor deviations dictated by operating practice, other variables were eliminated. The advantages resulting from the use of prepared ores included the following: (1) A 13.6% increase in iron production, (2) an 8% decrease in net coke consumption, (3) a 20% decrease in flux consumption, (4) a 9.3% decrease in flue dust and sludge production, (5) a 31.6% decrease in unrecovered metallics, (6) a 2.1% increase in the amount of wind blown per minute, and (7) a 10.2% decrease in the amount of wind blown per ton of iron produced.

Some Properties of Engineering Iron Powders. C. J. Leadbeater, L. Northcott, and F. Hargreaves. (Iron and Steel Institute, 1947, Special Report No. 38). The properties of 28 commercial iron powders, together with those of compacts prepared from them by a simple pressing and sintering technique, have been determined. The majority of the powders were prepared by either the oxide-reduction or electrolytic methods, but individual samples of the carbonyl, abrasion, and chloride-reduction methods were included.

At the outset of the investigation it became necessary to standardize or to develop methods of testing; these are described in Part I. The techniques for determining the particle, apparent, and tap densities of the powders, and the densities of the sintered compacts have been examined. The tap densities were found to vary with the method of tapping or vibration. The flow behaviour has been assessed by means of a coefficient determined by using cones with different orifices and weights of the powder sample; the effect of a cone stem on the rate of flow has been

demonstrated. Modification of the air-permeability method for the determination of specific surface has been found necessary for coarse powders. Surface texture, particle size, shape factor, and crystal structure have been studied by micro-examination, and the oxygen, hydrogen, and nitrogen contents have been determined.

In Part II. of the paper are described the properties of commercial powders, and the following ranges were found: Shape factor, 1.06–1.76; particle density, 7.26–7.89 g./c.c.; apparent density, 0.97–3.40 g./c.c.; tap density, 1.09–4.29 g./c.c.; flow coefficient, 1.24–>6.4; median size, 6–114 μ ; specific surface, 265–5161 sq. cm./g.; density after pressing at 30 tons/sq. in., 4.54–6.32 g./c.c.; compression ratio, 1.34–5.31; iron content (by difference) 96.70–99.64%; oxygen content, 0.10–2.09%.

The electrolytic iron powders are, in general, purer, softer in the annealed condition, and have slightly greater compressibility, than the oxide-reduced type, although both types show wide variation in properties.

The properties of sintered compacts are described

in Part III. The compacts were prepared by pressing at 30 tons/sq. in., and sintering in hydrogen for 1 hr. at 1050° C. The properties determined extended over the following ranges: Tensile strength, 4.09–20.07 tons/sq. in.; yield point, 2.0–13.1 tons/sq. in.; elongation, 0–8.3%; diamond pyramid hardness, 22.5–113; density, 4.60–7.05 g./c.c.; volume shrinkage, –1.56 to + 27.0%.

Electrolytic iron powders yield compacts having, on the average, slightly lower tensile strength and higher elongation than the oxide-reduced powders.

The results are considered in Part IV. and additional data are adduced. A large number of simple correlation coefficients have been computed for the properties considered. It is clear that many factors contribute to the behaviour of a powder when it is pressed and sintered, and the properties of the compact are not dependent solely upon any one property of the powder. Further tests show that among the more important requirements for high tensile strength are small particle size and freedom of the surface of the particles from oxidation.

FOUNDRY PRACTICE ·

(Continued from pp. 110 A–111 A)

A Program for Foundry Training. F. W. Hurt. (Foundry, 1946, vol. 74, Sept., pp. 72–75, 158–162). The training scheme for foundry apprentices and semi-skilled foundry employees developed by an American company producing iron castings is outlined.

Planned Lighting for the Modern Foundry. W. H. Kahler. (Foundry, 1946, vol. 74, Oct., pp. 82–85, 226–228). An analysis of the problem of providing adequate and efficient lighting in a foundry is made with recommendations on the minimum illumination required for various operations.

The Stability of Iron Carbide. L. Crome. (Foundry, 1946, vol. 74, Sept., pp. 90–91, 128–130). The stability of iron carbide in malleable cast iron is discussed, and experiments in which the malleablizing treatment was repeated several times are described. In the first treatment carbon nodules were dispersed in a matrix of ferrite grains and all the carbide was decomposed. On repeating the treatment six to eight times in either carburizing or decarburizing gases, carbides again formed and these were much more stable than the initial carbides.

Annealing Ore. (Iron and Steel, 1946, vol. 19, Nov., pp. 615–616). A brief description is given of the preparation, at Egremont, Cumberland, of special haematite ore for use in annealing malleable cast iron.

The Scope of Bentonite in the Foundry. A. W. Ulmer. (Institute of Australian Foundrymen: Australasian Engineer, 1946, Sept. 7, pp. 39–46). The molecular structure of montmorillonite and kaolinite are described. The differences in them account for the difference in behaviour on wetting. The properties of the sodium-type montmorillonite,

usually known as bentonite, and its effect on the green and dry strengths of natural and synthetic moulding sands, are discussed in detail. The compositions of synthetic-sand mixtures used for iron and steel castings in Australia are given and methods of testing sands are described.

A Simple Rapid Method for Determining the Moisture Content of Sand. P. D. Liddiard and Elizabeth Seal. (Foundry Trade Journal, 1946, vol. 80, Nov. 14, pp. 257–260, 271). An illustrated description is given of a method of moisture determination which employs electrical resistance measurements. The main advantage claimed is rapidity, obtained at the expense of accuracy, since it is considered that a number of less accurate determinations are more useful than one obtained by the usual methods which may not be representative of the sand pile under consideration. The instrument may be adapted for the regulation of water additions in a continuously circulating sand system.

Permanent Mold Gray Iron Castings. E. C. Hoenicke. (Materials and Methods, 1946, vol. 24, Oct., pp. 901–904). A process developed by the Eaton Manufacturing Company for the continuous production of grey iron castings in mechanically operated permanent metal moulds is described in detail, with illustrations. Advantages claimed for the product over sand castings are absence of surface-hardness and scale, uniform structure with fine graphite, freedom from porosity, and ability to withstand the pressure of liquids and gases.

Jobbing Work in an Indian Foundry. S. G. Athanikar. (Institute of British Foundrymen: Foundry Trade Journal, 1946, vol. 80, Oct. 31, pp. 209–212). A description, with diagrams, is given

of the method used in an Indian foundry for the moulding of a 3-ft. dia. cast-iron pipe bend, and its guide-vane piece.

Foundries—Notes on German Iron and Steel Foundries Including Centrifugal Casting. (British Intelligence Objectives Sub-Committee, 1946, Final

Report No. 818: H.M. Stationery Office). Reports are presented of visits to the foundries of six German firms making a variety of iron and steel castings including ingot moulds, white-heart malleable iron pipe fittings, gun barrels (centrifugally cast), high-silicon iron castings, bath tubs, and spun pipes.

PRODUCTION OF STEEL

(Continued from pp. 111 A–112 A)

Technics of Soviet Iron and Steel Industry. I. Bardin. (Metallurgia, 1946, vol. 34, Oct., pp. 325–326). A brief survey is made of the destruction caused by the war in the Russian iron and steel industry. The progress already made in reconstruction under the new five-year plan is considerable, and by 1950 it is planned to increase the annual output of pig iron, steel, and rolled steel by 35% above the total for the last pre-war year 1940. Production is to be increased by fuller and more economical use of raw materials, improvements in mining and transportation, beneficiation of ores, development of scrap-metal recovery, the building of more modern furnaces and rolling mills, and the extension of scientific research.

Steelworks Layout. G. A. V. Russell. (Staffordshire Iron and Steel Institute: Iron and Steel, 1946, vol. 19, Sept., pp. 521–527; Oct., pp. 555–560). See p. 71 A.

Gas and Air Port Blocks. J. R. Rait. (Iron and Steel, 1946, vol. 19, Oct., pp. 543–548; Nov., pp. 587–589, 616). The refractories available for constructing the port blocks of acid open-hearth furnaces are incapable of withstanding the high temperatures and the fluxing action of the iron-oxide dust during melting operations. The limitations of siliceous jointing cements are discussed, modern trends of thought regarding revolutionary furnace design and new types of super-duty refractories are outlined, and a new method for the construction of gas and air port blocks, which facilitates hot repairs and eliminates failures due to fluxing is described.

Mixed Fuels in Open Hearth Furnaces. J. C. Foster. (Iron and Steel Engineer, 1946, vol. 23, July, pp. 88–91). An account is given of the fuel control system for the open-hearth melting shop of the Bethlehem Steel Company where the furnaces have one burner for mixed blast-furnace and coke-oven gas and a second burner for oil placed below the gas burner. The fuel consumption and costs are discussed.

Some Theoretical Aspects of Heat Transfer in Open Hearth Steel Practice. P. T. Carter. (Journal of the West of Scotland Iron and Steel Institute, 1944–45, vol. 52, Part V., pp. 89–101). The theoretical aspects of the transfer of heat by radiation in the open-hearth furnace are discussed. The amount of radiation from both luminous and non-luminous flames depends not only on the emissivity but also on the temperature attained. For a given fuel, the temperature is lower when the flame produced is luminous, but this is offset by the higher emissivity of the luminous flame; an optimum condition will, however, be reached

beyond which further imperfection of the combustion will reduce the resulting radiation. This optimum condition depends on the fuel, the amount of pre-heat, and the type of burner used; in a given case it can be determined only by experience. The only theoretical method of increasing flame temperature for a given fuel without lowering its luminosity would be to replace the air used by oxygen, for a very large proportion of the heat evolved is employed in raising the temperature of the nitrogen in the air supply to the temperature of the flame. Calculations are made to determine the effect of substituting either oxygen for air, or methane for producer gas, on the flame temperature, and therefore on the rate of heat transfer in an open-hearth furnace when the charge is at 1000° C., alternatively at 1550° C. Taking the rate of heat transfer to the charge using producer gas and air (both preheated to 1000° C.) to be 1.0, this rate is increased by using cold methane and air at 1000° C. to 1.35 and 1.5 for charges at 1000° and 1550° C. respectively. Using oxygen, these rates are increased still further to 2.1 and 2.4 respectively; whilst with cold air and cold methane the rates are decreased to 0.51 and 0.35 respectively.

Practical Interpretation of Theoretical Steel Making for the Benefit of Management and Operator. C. F. Christopher. (Blast Furnace and Steel Plant, 1946, vol. 34, May, pp. 587–591, 607–609; June, pp. 715–720; Aug., pp. 990–994). In the first part of this paper the interactions of carbon, manganese, and silicon with the metal and the slag in the presence of iron oxide in an open-hearth furnace and the measure of control which the furnace operator can exert over the reactions are considered in detail. In the second and third parts the stresses arising as steel cools in the ingot mould are discussed and related to the different types of ingot defects and the carbon content of the steel.

Some New Devices at Alan Wood Steel Company. J. W. Deimler. (Iron and Steel Engineer, 1946, vol. 23, Sept., pp. 110–111). Two new automatic devices for the melting shop are described. The first is the mechanism for actuating a recording weighing machine for cars carrying loaded charging boxes. The second is an infra-red heating installation for heating 55-gal. drums of tar to 150–160° F. to prepare it for coating the walls of ingot moulds.

The Treatment of Waste Waters from the Steel Industry. C. L. Siebert. (Iron and Steel Engineer, 1946, vol. 23, July, pp. 78–83). Methods of treating waste water and spent liquor from iron and steel works are reviewed. The liquids dealt with include

pickling liquor, cyanide solutions from heat-treatment plants, water from blast-furnace-gas washers, waste lubricating oils, cutting compounds, and water containing phenols from by-product plants.

Work Light for Steel Mills. D. H. Tuck. (Iron and Steel Engineer, 1946, vol. 23, Sept., pp. 80-81). The mechanics of seeing are explained and data on the strength of illumination required for various

operations in a steelworks are presented and discussed.

Lighting Systems—Their Maintenance and Improvement. B. F. Fantone. (Iron and Steel Engineer, 1946, vol. 23, Sept., pp. 77-79). The maintenance of lighting systems in iron and steel works is discussed and the costs of maintaining a 1000-W. incandescent lamp and a 3000-W. mercury-vapour lamp are compared.

REHEATING FURNACES

A New Soaking Pit Design. N. J. Urquhart. (Iron and Steel Engineer, 1946, vol. 23, July, pp. 101-102). A brief description is given of a new type of soaking pit which has neither regenerators nor recuperators; it is designed to have a maximum ingot-heating capacity for a given area of floor space.

Soaking Pit Operation. D. M. McGeary and R. D. Hindson. (Blast Furnace and Steel Plant, 1946, vol. 34, June, pp. 721-726; July, pp. 861-865; Aug., pp. 986-989). The development of soaking-pits is reviewed and the advantages and disadvantages of the reversing regenerative and the bottom-fired recuperative types are compared—the authors preferring the latter. A detailed description of the soaking pits at the works of The Steel Company of Canada and their operation and maintenance is given. This plant consists of fourteen Amco pits and eight regenerative pits.

Lukens Telescopic Stiff-Leg Soaking Pit Crane. J. S. Morris. (Iron and Steel Engineer, 1946, vol. 23, Sept., pp. 102-105). Owing to the special conditions at the soaking-pit building of the Lukens Steel Company which limited the height of the crane, an ingot crane to serve the pits had to be designed to incorporate a telescopic leg. Drawings and a des-

cription of this crane are presented. The leg is unique in that it is hollow, rectangular, telescopic, and can be rotated.

Gear Ratios on Bridge Drives of Cranes. H. H. Angel. (Iron and Steel Engineer, 1946, vol. 23, Sept., pp. 106-107). Details are given of the changes which were made to the gear ratios in the drives of a soaking-pit crane, an annealing-plant crane, and a charging machine.

Rotary Hearth Furnaces. J. H. Loux. (American Iron and Steel Engineers' Convention: Iron and Steel, 1946, vol. 19, Jan., pp. 41-44; Feb., pp. 85-88). The advantages of using rotary-hearth furnaces are discussed and five applications of this type of furnace are described and illustrated.

Rapid Heating of Steels. F. O. Hess. (Iron and Steel Engineer, 1946, vol. 23, Apr., pp. 73-80). The design of gas burners for furnaces is discussed with special reference to radiant burners in which the gases heat a cup-shaped refractory surface to incandescence and heat is radiated from a comparatively large surface to the charge. The advantages of this system are pointed out and examples of the rapid heating possible with sets of these burners built into a furnace wall are described.

FORGING, STAMPING, AND DRAWING

(Continued from pp. 112 A-113 A)

Manufacture of 155 mm. Steel Forgings. W. F. Jones. (Iron and Steel Engineer, 1946, vol. 23, July, pp. 92-100). A description is given of the layout of plant and equipment for the mass production of hollow shell forgings 155 mm. in dia. from solid billets. The plant includes a 1200-ton press for breaking the nicked billets into short blanks, four rotary-hearth furnaces, descaling machines, a piercing press, and roller-type draw benches. Special manipulators and trays for lifting and moving the forgings were designed so as to increase production.

High Speed Forging Increases Auto Parts Production. H. Chase. (Steel, 1946, vol. 119, Oct. 21, pp. 98-99, 134-136). An illustrated description is given of high-speed forging presses and other equipment for the mass production of connecting rods, rear axles, and other automobile parts.

Lubrication of Reciprocating Steam Engines and Steam Hammers. F. C. Schoen. (Iron and Steel, 1946, vol. 23, Sept., pp. 90-91). Recommendations

on the types of oil to use for various parts of reciprocating steam engines and steam hammers are made.

Basic Dies for Deep Drawing. C. A. Gray. (Machinist, 1946, Nov. 9, pp. 1230-1232). Examples are shown of the use of dies for the single-action, double-action, and "push-through" deep-drawing processes.

Steel Wire—Notes on German Wire Drawing and Steel Rope Manufacture. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 823: H.M. Stationery Office). Reports of visits to four German firms making wire and wire rope are presented. One firm specializes in drawing stainless and high-speed steels and notes were made on the cleaning, drawing, and polishing of stainless rod. Descriptions are given of the organization and testing equipment at the official wire-rope testing station at Bochum with special reference to the electromagnetic testing of ropes for broken strands, and the fatigue-testing of wire ropes.

ROLLING-MILL PRACTICE

(Continued from p. 113 A)

Tables of Rolling Pressures and Power Requirements for Rolling Steel Shapes. (Blast Furnace and Steel Plant, 1945, vol. 33, July, p. 846; Aug., p. 982; Sept., p. 1126; Oct., p. 1262; Nov., p. 1398; Dec., p. 1534; 1946, vol. 34, Jan., p. 130; Feb., p. 250; Mar., p. 370; Apr., p. 482; May, p. 594; June, p. 746; July, p. 866). A series of tables is presented giving the rolling pressures and power requirements for rolling billets, angles, and flats, the data and information being translated and compiled by F. Waldorf from "Walzwerkswesen" by J. Puppe and G. Stauber.

Applied Lubrication. M. Reswick. (Iron and Steel Engineer, 1946, vol. 23, Sept., pp. 85-89). The principles of lubrication are explained. Information on the composition of greases is given and recommendations on the types of grease to use in high speed and slow speed bearings are made. Finally, a testing machine for extreme pressure lubricants is described.

Additives in Oils. W. P. Kuebler. (Iron and Steel Engineer, 1946, vol. 23, Sept., pp. 89-90). Brief notes are made on the purposes of various addition agents to lubricating oils.

Lubrication of Ball and Roller Bearings. A. S. Murray. (Iron and Steel Engineer, 1946, vol. 23, Sept., pp. 92-97). Different designs of ball and roller bearings are described with notes on their applications and the types of lubricant required for each.

Centralized Lubrication Systems. W. M. Stilwell, jun. (Iron and Steel Engineer, 1946, vol. 23, Sept., pp. 98-99). The advantages of lubrication systems in which many points on a single machine are lubricated from one position are explained. A measuring valve for supplying measured amounts of grease to bearings is described.

The Steel Company of Canada, Ltd., Follows Modern Practice in Production of Slabs and Blooms. C. Longenecker. (Blast Furnace and Steel Plant, 1946, vol. 34, Aug., pp. 973-978). Descriptions are given of the 34-in. and 44-in. blooming mills, generating sets, mill motors, and auxiliary equipment for producing slabs and blooms at the Hamilton Works of the Steel Company of Canada, Ltd.

Flame Deseaming. (Iron and Steel, 1946, vol. 19, Oct., pp. 571-572). A brief description is given of an oxy-acetylene deseaming machine, installed at a rolling mill in South Wales, for removing surface defects from billets by burning off a layer of metal from $\frac{3}{8}$ to $\frac{1}{4}$ in. in depth. The machine carries four banks of burners, operated by remote control, to encompass the billet as it runs through at about 200 ft./min.; the four rows of burners impinge on the four sides of the billet. Working at 50 lb./sq. in. oxygen pressure and at a speed of 220 ft./min., the consumptions of oxygen and acetylene are 90 and 3.8 cu. ft./ton of steel, respectively.

HEAT-TREATMENT

(Continued from pp. 114 A-115 A)

Some Users' Experience with Lithium Atmospheres for Heat Treating. R. S. Burpo, jun. (Materials and Methods, 1946, vol. 24, Sept., pp. 622-625). Descriptions are given of several examples of heat-treatment installations in which an air-propane mixture is cracked in a gas-heated unit, cooled to remove some of the moisture, and passed through a small chamber kept at 1200-1500° F. containing two lithium cartridges. These cartridges consist of steel cups 3 in. in dia. \times 4 in. deep filled with a mixture of lithium chloride, lithium carbonate, and metallic lithium. The atmosphere can be changed from carburizing to neutral by a simple adjustment of the air/gas ratio. The approximate rate of carburization is : to a depth of 0.020 in. in the first hour, to 0.034 in. in the first 2 hr., and to 0.044 in the first 3 hr. Data on the gas consumption and cost are given.

Armour Plate—Notes on Gas Carburising Process Carried Out at Krupp A. G., Essen. (British Intelligence Objectives Sub-Committee, 1946, Final Report 790: H.M. Stationery Office). The furnace and auxiliary equipment in which gas-carburizing of armour plate had been carried out by Krupp A. G., Essen, are described. Plates from 100 to 400 mm. thick were treated. Two plates were set up in box

formation, the plates forming the top and bottom; the sides were bricked up and luted with loam. Chromium-nickel steel tubes 60 mm. in dia. were introduced through the sides for the carburizing gas to enter. The "box" was passed into the carburizing furnace where it was treated for eleven days at 990-1000° C. The hearth of the furnace, carrying the box, was run out and cooled in air for 30 min. It was then pushed back and cooling continued to 700° C. in $7\frac{1}{2}$ hr., after which the box was opened. This was followed by a grain-refining process consisting of reheating and quenching in oil. One side was then hardened by heating the plate with one side and the edges buried in moist sand, the top surface reaching 920° C. and the bottom surface 570° C. Finally, the top surface was sprayed for 135 min., and the bottom for 330 min.

Temperature Uniformity in Heating-Up Processes. M. P. Heisler. (Transactions of the American Society of Mechanical Engineers, 1946, vol. 68, July, pp. 493-502). The treatment of temperature-uniformity problems by the method first introduced by Paschkis is extended and enlarged. It is shown that uniformity calculations can be reduced to the solution of a simple trigonometric relation which can be readily solved and analysed. Standard Gurney-Lurie charts

for cylinders and spheres are given in a more complete form than is available at present.

Carbon Concentration Control. E. G. de Coriolis, O. E. Cullen, and J. Huebler. (American Society for Metals, Nov., 1946, Preprint No. 14). The principles of carbon control in the gas-carburizing process are discussed in detail. From theoretical considerations the most suitable atmospheres for commercial carburizing are determined, and studied in relation to the conventional iron-carbon diagram. It is shown that any desired carbon balance between gas and metal can be obtained if the complexities of gas composition and steel analysis are known and properly controlled.

Cooling after Carburizing. (Machine Shop Magazine, 1946, vol. 7, Oct., pp. 86, 88). An illustrated description is given of a furnace used for the "Homocarb" carburizing process. The furnace is electrically heated, and the carburizing gases are circulated by a fan to ensure a uniform temperature throughout. The load can be cooled in the furnace by circulating cool air in the space between the retort and the refractory wall, by means of natural convection, without any air coming in contact with the charge.

On the Decarburization of Steel and Related Questions. J. L. Snoek. (Physica, 1941, vol. 8, pp. 734-744; N. V. Philips' Gloeilampenfabrieken No. 1562). The existence of a ferritic boundary layer in decarburized steel is explained by the exceedingly high diffusion-velocity of the carbon in α -iron. The diffusion properties of carbon and of nitrogen into iron are similar. The diffusion velocity is rapid if the

gain in energy obtained by placing an atom from the diffusing element into its new surroundings is small or even negative. The low value of the solubility of carbon and nitrogen in the lattice, and the low chemical affinity for iron as determined by the author's measurements, indicates that the fit of the carbon and nitrogen particles in the α -lattice is a very bad one. As the rate of diffusion of one element into another is expected to be higher the worse the diffusing element fits into the basic lattice, this accounts for the rates of diffusion of carbon and nitrogen in the α -phase being so high.

Overheating and "Burning" of Steel. F. C. Thompson. (Iron and Steel, 1946, vol. 19, Oct., pp. 551-554). The author discusses the papers by Preece, Hartley, Mayer, and Nutting, and by Woolman and Kirkby on the overheating of steel (*see* Journ. I. and S.I., 1946, No. I., p. 44 A). From the evidence presented the conclusion is drawn that the process of manufacture is *of itself* unlikely to influence the temperature at which overheating begins. An important cause of deterioration at high temperatures is the reaction $\text{FeO} + \text{C} \rightleftharpoons \text{Fe} + \text{CO}$, as a result of which a gas is formed. The fact that an increase in the sulphur content raises the overheating temperature is due to the volume of SO_2 produced from a given amount of FeO on reaction with sulphur being only half of that of the CO resulting from the corresponding reaction with carbon. There is strong evidence that a high overheating temperature and a high inclusion count go side by side.

WELDING AND CUTTING

(Continued from pp. 115 A-117 A)

Contact Arc-Welding. P. C. van der Willigen. (Philips Technical Review, 1946, vol. 8, June, pp. 161-166). An account is given of the development of "contact" electrodes, and their properties. When welding with this electrode the end is kept in continuous contact with the work. In the electrode, half the metal of the core is carried in powder form in the coating and the outside diameter is more than double the diameter of the core. Ignition of the arc is automatic and can be done by pressing a button in the electrode holder. Much less skill is required to produce an even deposit in horizontal, vertical, and overhead welding with this contact electrode.

Practical Importance of Hydrogen in Metal-Arc Welding of Steel. S. A. Herres. (American Society for Metals, Nov., 1946, Preprint No. 30). A brief account is given of the sources from which hydrogen can enter the molten weld metal and of the mechanism by which porosity and hydrogen embrittlement are produced. The fact that the degree of embrittlement depends upon the microstructure of the steel and the rate and temperature at which it is strained shows that a precipitation reaction is probably responsible. Methods for determining the specific effects of porosity and embrittlement due to hydrogen on the strength and cracking susceptibility of welds are discussed, and the use of a double T test piece for welding tests is suggested, since this represents the most

severe conditions of restraint usually encountered in industrial fabrication.

Atomic Hydrogen Welding. (Aircraft Production, 1946, vol. 8, Apr., pp. 170-171). Details and illustrations are given of the use of the atomic hydrogen welding process in the manufacture of press tools and in the repair of broken tools. A punch and die can be made from a single piece of mild steel plate by flame-cutting and grinding, followed by the deposition of high-carbon tool steel with an atomic hydrogen torch. Compensation amounting to 40-50% is made for loss of carbon in the weld metal by using filler-wire of extra-high-carbon content. Appreciable savings are reported in labour and material costs as a result of repairs to broken or chipped machine tools by the deposition of molten tool steel.

Atomic Hydrogen Welding. I. H. Hogg. (Metropolitan-Vickers Gazette, 1945, vol. 21, Oct., pp. 117-125). The principles of atomic hydrogen welding are explained, and the equipment and technique are described with some examples of their application.

Effect of Recent Research on the Weldability and Control of the Production of Steel Aircraft Tubing. A. J. Williamson. (Welding Journal, 1945, vol. 24, Oct., pp. 485-S-496-S). A critical review is presented of the results reported by S. I. Hoyt, C. E. Sims and H. M. Banta in papers entitled "Improving the Weldability of High Strength, Low Alloy Steels"

and "Metallurgical Factor of Underbead Cracking" (see Journ. I. and S.I., 1945, No. II., pp. 121 A and 189 A, respectively).

Interpreting Spotweld Radiographs. R. C. McMaster. (Steel, 1946, vol. 119, Oct. 14, pp. 104-107). A series of 17 radiographs of spot welds in aluminium-clad steel sheet and aluminium alloy sheet is reproduced; these can be used as references for studying the quality of spot welds.

Thermit Welding in Steel Plant Maintenance. J. H. Deppeler. (Iron and Steel Engineer, 1946, vol. 23, Sept., pp. 55-62). The principles of thermit welding are explained and it is shown that although the weld metal is cast steel it makes an excellent weld with either forged or rolled steel. Several examples of heavy welds for steelworks plant maintenance are described and illustrated.

MACHINING

(Continued from p. 54 A)

The Determination of Machinability. G. Schlesinger. (Machinery, 1946, vol. 69, Oct. 3, pp. 425-430). The elimination of variables in machinability testing is discussed and a procedure is described by which 19 variables can be partly reduced and partly standardized, so that only the resistance to cutting, characterized as the machinability index, emerges as one numerical factor. A one-component cutting dynamometer for determining the machinability is described.

Machinability, Tool Life, and the Machine Tool. G. Schlesinger. (Machinery, 1946, vol. 69, Oct. 10, pp. 463-467). The elimination of variables in machining tests was explained in a previous paper (see preceding abstract). In this article it is shown how the tool shape can be standardized and how tool-life tests may be taken by the one-component tool dynamometer.

New Methods of Analysis of Machining Processes. M. E. Merchant and N. Zlatin. (Proceedings of the Society for Experimental Stress Analysis, 1946, vol. 3, No. 2, pp. 4-19). A study of the geometry and mechanics of chip formation has resulted in the development of new methods of analysing and testing machining operations which yield more information than is possible by the standard methods. These methods are described in detail. Theoretical results derived from test data are reviewed.

Investigation into the Design, Manufacture, and Inspection Technique of Aero Engine Gears. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 381; H.M. Stationery Office).

Metallurgical Practice in the Precision Cutting Tool and Gauge Plants in Germany. (British Intelligence Objectives Sub-Committee, 1945, F.I.A.T. Final Report No. 230; H.M. Stationery Office). A report is presented on visits to 14 German works manufacturing tools and gauges. Details are given of the metals used, methods of inspection, the heat-treatment, grinding, lapping methods, and the stabilizing treatment.

Mechanical Report on Precision Cutting Tool and Gauge Plants in Germany. (British Intelligence Objectives Sub-Committee, 1945, F.I.A.T. Final Report No. 121; H.M. Stationery Office).

Processing and Fabrication of Stainless Steel Sheet and Plate Products. Part VII. Machining of Chromium-Nickel Materials. H. S. Schaufus and J. R. Federline. (Steel Processing, 1946, vol. 32, July,

pp. 448-452, 464). Continuation of a series of articles (see p. 117 A). Recommendations are made on tool materials and design, cutting speeds, and cutting fluids for machining stainless steels.

High-Speed Steel with a Reduced Tungsten Content. K. Amberg. (Jernkontorets Annaler, 1946, vol. 130, No. 6, pp. 205-212). (In Swedish). The results are presented of drilling and turning tests using high-speed steel tools containing chromium, vanadium, and molybdenum with 3%, 6%, and 12% of tungsten, and in one case with no tungsten.

German Needle and Associated Industry. (British Intelligence Objectives Sub-Committee, 1946, Final Report No. 457; H.M. Stationery Office). The object of the visits here reported was to ascertain the latest German methods of manufacture in the needle and fishing-tackle industry.

Profile Milling and Tool-Grinding Machines, Deckel, Munich. (British Intelligence Objectives Sub-Committee, 1945, F.I.A.T. Final Report No. 653; H.M. Stationery Office). Detailed descriptions are given of two new German machine tools, namely, the profile milling machine KF-1, and the tool-grinding machine S-1.

A Method for Measuring Tool-Tip Temperature. B. A. Crowder. (University of Minnesota, Institute of Technology, 1946, Technical Paper No. 55). A thermocouple method of measuring the temperature of tool-tips in machining is described. It was used to investigate the effects of cutting speed, width and depth of cut, tool-nose radius, and type of material being cut, on the temperature developed, and the results obtained are presented and discussed.

Wet-Belt Machining. W. F. Schleicher. (Steel, 1946, vol. 119, July 8, pp. 94-95, 114-117). Wet-belt machining is a method of grinding, surfacing, or removing material by the cutting action of a processed cloth belt coated with an abrasive which travels over a hardened steel platen at 2500-4500 ft./min., the belt being cooled with a mixture of water and soluble oil. A description is given of the equipment for this process, and its advantages are discussed.

The Use of Carbide Tools. M. J. Jacquet. (Iron and Steel Institute, 1946, Translation Series, No. 287). This is an English translation of a paper which was published in Revue de Métallurgie, Mémoires, 1943, vol. 40, Aug., pp. 225-231. (See Journ. I. and S.I., 1946, No. I., p. 27 A).

PROPERTIES AND TESTS

(Continued from pp. 120 A-124 A)

The Strength of Grey Iron in Relation to Composition. H. T. Angus and J. G. Pearce. (Bulletin of the British Cast Iron Research Association, 1946, vol. 8, Nov., pp. 323-329). An investigation is described in which the strengths of grey cast irons of varying compositions were determined, when all other factors were standardized. For standard test bars a relationship is established between the carbon equivalent value (determined from the carbon, silicon, and phosphorus contents) and the tensile or transverse strengths. The results apply only to unalloyed grey irons not subjected to ladle treatment and with a carbon equivalent value above 3.7.

Testing Bolts for Strength and Ductility. D. E. Lehane. (Steel, 1946, vol. 119, July 22, pp. 86-87, 134-136). The following recommendations are made for the testing of bolts and nuts: (1) Instead of machining a standard specimen from the bolt shank a full-sized bolt should be used; (2) three turns of the screwthread should be included in the length between the grips of the machine; (3) in calculating the strength per square inch, the mean of the diameters of the root and the top of the thread should be used; and (4) the yield strength should be taken as the basis of the strength of the bolt.

Tension Testing at Elevated Temperatures. T. M. Blackmon, P. R. Nourse, and E. H. Plesset. (A.S.T.M. Bulletin, 1946, May, pp. 32-37). A simple and inexpensive method of heating tension specimens by resistance heating, a method of measuring specimen temperatures, two types of extensometers, and the associated electronic equipment for use with a Baldwin-Southwark recorder, have been developed and are described in this paper.

The Effects of Microstructure on the Mechanical Properties of Steel. J. H. Hollomon, L. D. Jaffe, D. E. McCarthy, and M. R. Norton. (American Society for Metals, Nov., 1946, Preprint No. 25). An account is given of the mechanical properties of two steels after several different heat-treatments. The steels used were S.A.E. 3135 (0.35% of carbon, 0.87% of manganese, 1.16% of nickel, 0.50% of chromium) and N.E. 8735 (0.34% of carbon, 0.95% of manganese, 0.66% of nickel, 0.56% of chromium, 0.24% of molybdenum). Specimens of the former were embrittled to varying degrees by heating at 450° C. for different lengths of time after annealing at higher temperatures. Specimens of the latter were treated to produce various as-quenched structures and then tempered. In each case, tensile, notched-bar impact, and fatigue tests were carried out. The reduction in area and ultimate tensile strength were the only tensile properties affected by changes in structure. The impact properties were very sensitive to structural changes, but fatigue properties were only affected to a limited extent. The tempered martensitic steels had mechanical properties superior in all respects to those having other structures.

Improved Guides for Positioning of Impact Specimens.

J. R. Speer. (A.S.T.M. Bulletin, 1946, Mar., pp. 46-47). Two forms of improved guides for holding the specimens in Charpy and in Izod impact testing machines are described.

Method of Notching Impact Test Specimens. S. E. Siemen. (A.S.T.M. Bulletin, 1946, Mar., p. 45). A description is given of a tool for machining the 45° notch on impact-test specimens.

Pole Figures of the Effect of Some Cold Rolling Mill Variables on Low Carbon Steel. J. K. Wood, jun. (American Society for Metals, Nov., 1946, Preprint No. 11). The large amount of data collected in an investigation of the orientation effects produced in cold-rolled low-carbon steel sheet is represented by means of pole figures. These figures illustrate quantitatively the results of varying (1) the total reduction at the end of each pass, (2) the roll diameter, (3) the duration of the pass, and (4) the tension on the strip. The pole-figure data were obtained from X-ray diffraction patterns using a technique developed by the author, details of which are given.

Hardness Testing of Metals and Alloys at Elevated Temperatures. F. P. Bens. (American Society for Metals, Nov. 1946, Preprint No. 3). A description is given of an apparatus constructed for accurately determining the hardness of metals and alloys at temperatures up to 925° C., using the diamond-pyramid penetration principles. It employs the stage, the loading device, and the optical system of a standard Vickers hardness machine. A vacuum chamber protects the specimen, diamond indenter, and heating element against oxidation. The data obtained with the apparatus indicate that there is a relationship between the hardness and the ultimate tensile strength at high temperatures.

The Tempering of High Alloy Tool Steels. G. A. Roberts, A. H. Grobe, and C. F. Moersch, jun. (American Society for Metals, Nov., 1946, Preprint No. 9). Tempering data are reported for eight high-alloy tool steels (three high-speed steels, three cold-work die steels, and two hot-work die steels). They cover the range of heat-treatment from 95° to 705° C. for from 0.1 to 100 hr., at least four quenching temperatures being used for each steel. Of the various methods of presenting the data which were used, the best was considered to be that of Hollomon and Jaffe, which is to plot the Rockwell "C" hardness against the parameter $T(C + \log t)$, where T is the absolute temperature of tempering, t is the time of tempering, and C is a constant for a given steel. The effect of quenching temperature on the quenched hardness of the high alloy tool steels is discussed.

The Measured Knoop Hardness of Hard Substances and Factors Affecting Its Determination. N. W. Thibault and Helen L. Nyquist. (American Society for Metals, Nov., 1946, Preprint No. 23). The factors influencing the measurement of the Knoop hardness number are discussed in detail, with particular reference to hard, brittle substances. The conditions believed to be necessary for the determina-

tion of the Knoop hardness number of such materials are specified. A table of typical Knoop-number determinations given includes those for a variety of materials ranging from boron carbide to tool steel.

Relation of Quenching Rate and Hardenability to the Mechanical Properties of Several Heat Treated Cast Alloy Steels. C. R. Wilks, H. S. Avery, and E. Cook. (American Society for Metals, Nov., 1946, Preprint No. 28). The available results of a study of the effects of quenching rate and of hardenability upon the mechanical properties of several heat-treated cast alloy steels are presented in this paper. To simulate the conditions obtaining at the centre of plates 2 to 8 in. in thickness, a double end-quench technique was used (*see* Journ. I. and S.I., 1945, No. 1, p. 58 A). Tensile and impact properties were determined, the latter proving most sensitive to the structural modifications brought about by hardening. The authors suggest that optimum mechanical properties are associated with the minimum hardenability which will produce the maximum hardening for any particular rate of cooling.

The Magnetic Hardness Testing of High-Speed Steels. H. Springer. (Iron and Steel Institute, 1946, Translation Series No. 293). This is an English translation of a paper which was published in *Zeitschrift des Vereines deutscher Ingenieure*, 1940, vol. 84, June 1, pp. 365-370. (*See* Journ. I. and S.I., 1946, No. I., p. 53 A).

Development of Temper Brittleness in Alloy Steels. W. S. Pellini and B. R. Queneau. (American Society for Metals, Nov., 1946, Preprint No. 16). The development of temper brittleness has been studied in two steels of different hardenability. The effects of isothermal heat-treatment in the range of temper brittleness have been determined and compared with the embrittlement developed in the steels while cooling or heating through the same range of temperatures. For one of the steels the influence of the microstructure on temper brittleness has been examined.

The transformation which causes embrittlement in alloy steels was found to be a reversible reaction. A maximum rate of embrittlement was reached at about 510° C., but a certain amount may occur at as high as 650° C. A pearlitic structure was rather less susceptible to temper brittleness than one of martensite or low-temperature bainite. It is suggested that carbide precipitation from α -iron is responsible for temper brittleness.

The Influence of Eddy Currents on the Apparent Hysteresis Loop of Ferromagnetic Bars. J. L. Snoek. (Physica, 1941, vol. 8, pp. 426-438; N. V. Philips' Gloeilampenfabrieken, No. 1545). The cause of slight errors which have occasionally been observed in measurements of the induction of soft magnetic materials in the form of bars or wire is discussed.

The Determining Factors of Permeability. J. L. Snoek. (Physica, 1941, vol. 8, pp. 344-346; N. V. Philips' Gloeilampenfabrieken No. 1539). Recent measurements of the crystal anisotropy of slowly cooled nickel-iron alloys by E. M. Grabbe as well as the results obtained by H. J. Williams and R. M. Bozorth with single crystals or iron and silicon-iron

confirm the conclusion reached by the present author in 1936 that the permeability of homogeneous fully annealed alloys is entirely dependent on the magnetostriction and the crystal anisotropy in conjunction with the crystalline structure. However, according to results obtained by G. Rathenau and the author when determining the permeability of cold-rolled nickel-iron alloys, the permeability cannot be even approximately related to the effects of internal stresses and the crystalline structure.

Effect of Small Quantities of Carbon and Nitrogen on the Elastic and Plastic Properties of Iron. J. L. Snoek. (Physica, 1941, vol. 8, pp. 711-733; N. V. Philips' Gloeilampenfabrieken No. 1561). The phenomenon of elastic after-effect in pure iron, commercial iron, and iron alloys, and its relation to the presence of nitrogen or carbon in solid solution is discussed, and experiments are described in which the damping capacity of very fine wires containing different amounts of the above elements was measured at temperatures in the range -50° C. to +100° C. All the materials tested, provided they had the cubic body-centred lattice, exhibited this phenomenon. The after-effect could be defined with sufficient accuracy by a single relaxation time τ which is identical with the value determined by magnetic methods. On changing the temperature the damping curve passed a maximum point. This applied only to fully annealed specimens. If the specimen had been cold-deformed the position of the maximum damping was displaced to a higher temperature; this is the damping described by W. S. Gorski. A new theory to account for the first maximum is offered.

The Stress Rupture and Creep Properties of Heat Resistant Gas Turbine Alloys. N. J. Grant. (American Society for Metals, Nov., 1946, Preprint No. 2). A large number of tensile and creep tests at temperatures between 815° and 980° C. on heat-resisting alloys are reported. These included several non-ferrous alloys, chromium irons, and nickel-chromium stainless steels. Attention was directed mainly towards determining the effects of variations in carbon and nitrogen content on the hot strength and ductility of the alloys; the influence of heat-treatment and ageing; and the relationship of the stress to the rupture time and to the minimum creep rate as measured in both tensile and creep tests. An important relationship was shown to exist between the time at which the alloys were maintained at a specified temperature and the resultant ductility of the alloys at fracture. The surface condition of the precision-cast test bars was shown to have some effect on the rupture strength. The tensile strengths of representative alloys were measured at atmospheric temperature, when in the as-cast, heat-treated, and/or aged conditions. The alloys high in carbon were the stronger up to a peak carbon value beyond which the strength decreased. Structural changes with increasing carbon content are shown in photomicrographs. The most suitable microstructure for high strength is indicated.

The Apparent Influence of Grain Size on the High Temperature Properties of Austenitic Steels. C. L. Clark and J. W. Freeman. (American Society for Metals, Nov., 1946, Preprint No. 19). This paper presents

the results of an investigation undertaken to determine the effects of variations in grain size on the properties at high temperatures of austenitic steels. The four steels used were an 18/8 chromium-nickel, an 18/12 chromium-nickel with columbium additions, a 25/20 chromium-nickel, and a 25/12 chromium-nickel steel. Short-time tensile, creep, and stress-rupture tests were carried out at temperatures up to 980° C.

It is shown that too broad generalizations cannot be drawn with respect to the influence of grain-size variations on the high-temperature properties. The coarser grain structures in the 18/8 alloy were slightly superior to the finer ones at the more elevated temperatures. Over certain parts of the temperature range, the tensile strengths of the other three steels in the fine-grained condition were greatly inferior to their strengths when coarse-grained, but they possessed a much greater ductility under prolonged stresses. It is concluded that the choice of the proper grain size depends on the proposed operating temperature and the relative importance of strength and ductility under prolonged periods of time.

Changes in Size and Toughness of High Carbon-High Chromium Steels Due to Subzero Treatments. L. E. Gippert and G. M. Butler, jun. (American Society for Metals, Nov., 1946, Preprint No. 10). Three types of high-carbon high-chromium die steels are shown to expand considerably when given a subzero treatment after hardening, but before tempering. Hardnesses of Rockwell C 67 to 68 were produced. Less expansion was caused when the steels were held at room temperature for 24 hr. before the cold-treatment, and tempering at 150° C. almost entirely nullified the effect of subsequent cold-treatment. Izod impact tests did not reveal any excessive increase in brittleness when allowance was made for the increased hardness.

The Effect of Manganese on the Properties of Cast

Carbon and Carbon-Molybdenum Steels. N. A. Ziegler, W. L. Meinhart, and J. R. Goldsmith. (American Society for Metals, Nov., 1946, Preprint No. 27). The results of an investigation on the effect of manganese on the thermal characteristics, microstructures, physical properties, and weldability of plain carbon and carbon-molybdenum cast steels are presented. Increases in the manganese content of these steels cause a gradual increase in the thermal sluggishness and hardenability, which is less pronounced than that occurring with molybdenum or nickel additions to chromium steels. At least 2% of manganese is needed to promote marked air-hardening and the suppression of transformations on slow cooling. Manganese exerts a greater effect in this respect on the carbon-molybdenum and higher carbon steels. A manganese content of 1.5% in plain carbon steel, and 1% in carbon-molybdenum steels increases the tensile strength by 20% compared with similar steels with a manganese content of 0.5%, and gives very high impact resistance properties. No difficulties are encountered in welding steels with less than 2% of manganese.

Ferritic Discs for Gas Turbines. D. A. Oliver and G. T. Harris. (Metallurgia, 1946, vol. 34, Oct., pp. 293-295). The composition and properties of four brands of ferritic steels developed for use in gas turbines are given, and the use of such steels in the manufacture of turbine discs is briefly described.

Drop Forgings for Gas Turbine Application. C. I. Schweizer. (Materials and Methods, 1946, vol. 24, Sept., pp. 642-645). Alloy steels for making forged gas-turbine rotors are described and their forging properties discussed. These materials include chromium-nickel-molybdenum alloys, some with a small addition of tungsten. After forging, a stress-relieving treatment at 1200° F. is required.

METALLOGRAPHY AND CONSTITUTION

(Continued from p. 124 A)

A Metallographic Etchant to Reveal Temper Brittleness in Steel. J. B. Cohen, A. Hurlich, and M. Jacobson. (American Society for Metals, Nov., 1946, Preprint No. 17). Metallographic etching reagents and procedures are described which are capable of differentiating between the tough and temper-brittle conditions of steels susceptible to temper brittleness. The most successful reagent was one composed of an aqueous solution of picric acid and "Zephiran Chloride" (a mixture of alkyl-dimethylbenzyl-ammonium chlorides). This made a pronounced attack on the grain boundaries of steels embrittled either by slowly cooling from elevated temperatures or during tempering at intermediate temperatures, but did not affect steels in the tough condition or those not susceptible to temper brittleness. The above reagent is also of use for the determination of inherent austenitic grain size in alloy steels which can be embrittled.

New Etching Reagents for Iron and Steel. R.

Pusch. (Iron and Steel Institute, 1946, Translation Series, No. 292). This is an English translation of a paper which was published in Archiv für das Eisenhüttenwesen, 1940, vol. 14, July, pp. 15-25. (See Journ. I. and S.I., 1941, No. II., p. 226 A).

A Periodic Chart for Metallurgists. C. A. Zapffe. (American Society for Metals, Nov., 1946, Preprint No. 12). A periodic chart of novel design is illustrated which has, in addition to the relationships portrayed by the table of Mendeleeff, the following characteristics: (1) The chart consists of a schematic cross-section of the electron shell of the heaviest atom and it has all the elements so placed that, for any one of them, the elements of lesser atomic numbers depict the number of electrons in that atom, and their position in the principal and sub-shells; (2) analogous properties of the elements appear along radii, along diameters, along shell peripheries, and within the separate sectors. A series of alloy systems of metallurgical interest are presented, based on this chart, which

show the characteristic patterns that result from its use. It is considered that these may help in understanding certain principles governing metallurgical phenomena, and serve as a useful means for predicting the characteristics of new alloy systems.

Stability of Austenite in Stainless Steels. C. B. Post and W. S. Eberly. (American Society for Metals, Nov., 1946, Preprint No. 5). An account is given of an investigation into the stability at room temperature of austenite in nickel-chromium stainless steels, in which the change in magnetic permeability of the austenite was measured after cold-reduction. Through the range of analyses used (chromium 13.90% to 24.30%, nickel 7.75% to 20.65%, carbon 0.03% to 0.20%, manganese 0.40% to 3.92%, molybdenum up to 2.40%, columbium up to 1.0%, and titanium up to 0.50%), the steels were austenitic and non-magnetic after annealing at above 1000° C.

At constant cold-reduction, the tensile strength of fairly stable austenitic steels (*i.e.*, those requiring approximately 80% cold-reduction to precipitate measurable quantities of pseudo-martensite) was found to be a function of the carbon contents. An empirical formula was developed for estimating the nickel content required to make a chromium-nickel steel substantially stable (requiring 80% cold-reduction to cause a noticeable change in magnetic properties). The difference between this theoretical and the actual nickel content was evaluated as a factor Δ , which is a measure of the stability. Since carbon, manganese, and molybdenum have a marked effect on the stability of the austenite, the formula takes these elements into consideration.

Changes in Austenitic Chromium-Nickel Steels During Exposures at 1100° to 1700° F. P. Payson and C. H. Savage. (American Society for Metals, Nov., 1946, Preprint No. 18). A description, illustrated with micrographs, is given of a study of four types of high-alloy nickel-chromium steels, with varying silicon contents and additions of nitrogen, columbium, titanium, and zirconium. The steels were given long isothermal treatments at temperatures between 595° and 925° C., which caused the formation of a sigma phase (hitherto incompletely identified), usually associated with precipitated carbides. High percentages of chromium, silicon, and nitrogen, and additions of columbium, titanium, and zirconium promoted the formation of this new phase, for the metallographic identification of which a scheme is given.

Factors Influencing the Pearlitic Microstructure of Annealed Hypoeutectoid Steel. R. A. Grange. (American Society for Metals, Nov., 1946, Preprint No. 26). A description is given of the pearlitic structures developed by the similar isothermal annealing (at temperatures not more than 100° F. below the A_{e1} point) of twelve types of hypo-eutectoid steel killed with aluminium. The character of the pearlite varied with the composition and was classified in two general groups, well-formed lamellar pearlite, and "semi-pearlite" in which the carbides were relatively coarse and non-lamellar. The general conclusions reached were: (1) In the steels containing chromium, the structure was well-formed pearlite, whereas in those without chromium it was massive,

non-lamellar carbide; (2) the pearlite was substantially lamellar in specimens which had coarse austenite grains just before transformation, whether the coarseness was due to lack of de-oxidation with aluminium, high austenitizing temperature, or to heating after cold working; (3) in plain carbon, nickel, or nickel-molybdenum steel, when the transforming austenite was fine-grained, the pearlite formed was only partly lamellar, most of the carbide being present as scattered particles. This "semi-pearlitic" type of structure is a direct product of transformation of austenite and not the result of coalescence of initially lamellar carbides; (4) in steels of a composition prone to non-lamellar carbide formation, well-formed pearlite can be produced, even if the austenite be fine-grained, if aluminium is not used for killing. It is suggested that the mode of formation of the carbides in annealed hypo-eutectoid steels is associated with the fineness of grain of the austenite and the fundamental factors which influence this grain size.

Recrystallization in Rolled Nickel-Iron. J. F. H. Custers and G. W. Rathenau. (Physica, 1941, vol. 8, pp. 759-770; N. V. Philips' Gloeilampenfabrieken, No. 1564). The mechanism of the recrystallization of heavily reduced sheets of aluminium, copper and nickel-iron alloys is discussed. Small additions of some elements, *e.g.*, phosphorus, prevent nickel-iron and copper from recrystallizing in cube orientation. The recrystallization texture of a pure 48/52 nickel-iron alloy depends on temperature. A study of this showed that after recrystallization at about 900-1000° C. the cubic crystals contain twins which disappear at still higher temperatures.

Magnetic Anisotropy in Cold-Rolled Nickel-Iron. G. W. Rathenau and J. L. Snoek. (Physica, 1941, vol. 8, pp. 555-575; N. V. Philips' Gloeilampenfabrieken No. 1552). Nickel-iron alloys containing more than 30% of nickel can be brought into a state called "the pseudo unicrystalline state" by a process of severe cold-rolling followed by recrystallization at a high temperature. If a strip of such an alloy is again cold-rolled in the same direction, or in a direction at 90° to it, the material becomes highly anisotropic. Experiments investigating this anisotropy are described.

The Chromium-Oxygen Equilibrium in Liquid Iron. Hsin-Min Chen and J. Chipman. (American Society for Metals, Nov., 1946, Preprint No. 7). Experiments are described in which liquid iron-chromium alloys containing up to 20% of chromium were brought into equilibrium with accurately controlled gaseous mixtures of water vapour and hydrogen. Equilibrium constants and free energy changes were measured for the liquid/gas reactions, and these were found to be in agreement with figures obtained by extrapolation of results at lower temperatures.

Experimental Studies of Continuous Cooling Transformations. C. A. Liedholm. (American Society for Metals, Nov., 1946, Preprint 21). This paper demonstrates the methods, results, and applications of experimental studies of continuous cooling transformations. Experimental results are presented on the mechanical and physical properties of hypo-eutectoid steel subjected to partial transformations in Jominy

end-quench tests and in tests on flat end-quenched bars. Ferrite rejection during continuous cooling may increase the time required for a subsequent isothermal transformation in the bainite region by as much as 2000%.

Isothermal Transformation of Austenite. A. Hultgren. (American Society for Metals, Nov., 1946, Preprint No. 22). The results of a study of isothermal transformations in manganese and tungsten steels are given in the form of time-temperature-transformation diagrams. A theory is developed on the hypothesis that the ferrite of pearlite and the carbide of bainite each has a so-called secondary orientation in the parent austenite differing from the so-called primary orientation of the same constituents in the other of the two transformation products. It is suggested that, in alloy steels, while pearlite is formed according to the laws of a binary eutectoid reaction in a ternary system, reaching an equilibrium known as the "ortho-equilibrium," the alloying element does not take part in the bainite reaction, the ferrite and carbide of which inherit their alloy contents from the austenite. This gives rise to the metastable "para-equilibrium." The analysis of carbide residues bears out the hypothesis. The nucleation of a precipitate in a supersaturated solid solution is considered to start, not from

local accumulations of atoms caused by random fluctuations, but from chance formations of minute regions of the new lattice, called "embryos," the growth of which to stable nuclei and larger structures is a continuous process made possible by diffusion super-imposed on random fluctuations.

Transformations in Krupp-Type Carburizing Steels. A. R. Troiano and J. F. De Moss. (American Society for Metals, Nov., 1946, Preprint No. 24). An investigation is described of the transformation characteristics of a low-carbon and a high-carbon 1.5/4.0 chromium-nickel carburizing steel. The low-carbon steel represented a core, and the high-carbon steel a carburized case. The austenitizing temperatures used were approximately those of commercial practice. The established linear relationship between the carbon content of austenite and the axial ratio of tetragonal martensite formed from it was used to establish the temperature at which carbides first begin to precipitate. X-ray diffraction measurements showed that the axial ratio remained constant until the carbon content of the austenite was altered by carbide formation. The general features of the transformations are discussed in relation to the behaviour of other alloy steels.

CORROSION OF IRON AND STEEL

(Continued from pp. 81 A-83 A)

A Review of Factors Affecting the Corrosion of Iron and Steel Used in Building. D. W. James-Carrington. (Journal of the Institution of Structural Engineers, 1946, vol. 24, Sept., pp. 449-499). As it is impossible for a building designer to study all the literature on corrosion problems, the author considers it preferable to bring the fundamental aspects of corrosion before him. The author accordingly selects and presents such information as is necessary for a broad understanding of the principles underlying the protection of iron and steel used in building. The review is limited to the behaviour of ferrous materials when exposed to the atmosphere.

Effect of Heat Treatment on Corrosion Resistance. (Alloy Casting Bulletin, 1946, Jan., pp. 1-4; Apr., pp. 1-6; Aug., pp. 1-5). Investigations of the effect of heat-treatment of stainless steel castings on their resistance to corrosion in nitric acid are reported. The relation between composition, quenching temperature, and corrosion rate is dealt with in Part I. Depending on the composition, it is possible to quench-anneal from a comparatively low temperature and produce alloys which show a desirable carbide-free structure. In Part II, the relation of composition and temperature to the rate of carbide solution, formation, and agglomeration is considered. It is shown that carbides will dissolve in 1 min. at 2000° F. in alloys containing 0.12% of carbon. Consequently it may often be more economical to heat-treat at a high temperature for a short time than at a relatively low temperature for a longer period. In Part III, investigations to determine the sub-surface cooling

rates of large cast sections are reported. The results obtained provide a link between the data given in Part I, relating to test specimens and the results to be expected in castings of commercial size.

Behavior of 18-8 Ti-Stabilized Stainless. E. H. Wyche. (Iron Age, 1946, vol. 158, Aug. 8, pp. 61-65; Aug. 15, pp. 54-56). Methods of detecting and combating intergranular corrosion in 18/8 stainless steel are discussed. The effects of additions of the stabilizing elements titanium and columbium are also considered with notes on the calculation of the optimum ratio in which these elements should be added. In the second part of the paper information on the weldability, corrosion resistance, and stabilizing heat-treatment of this steel is given.

Overvoltage and Its Significance in Corrosion. S. Glasstone. (Corrosion and Material Protection, 1946, vol. 3, June-July, pp. 15-18). Overvoltage is the difference between the potential at which a gas, especially hydrogen, is evolved from a solution and the potential of a reversible electrode of the same gas in the same solution. The influence of overvoltage on the corrosion of metals is discussed. A metal of low overvoltage can increase corrosion, whereas a metal of high overvoltage may be used to inhibit the corrosion of a base metal. The bearing of over-voltage on the corrosion of tinsplate and on the occurrence of "hydrogen swells" is also dealt with.

The Use of Magnesium Anodes for Cathodic Protection. L. M. Oldt. (Corrosion and Material Protection, 1946, vol. 3, June-July, pp. 12-14). In

cathodic protection either a galvanic or an electrolytic anode is used. The galvanic anode consists of a metal higher in potential than the metal to be protected. Magnesium, which combines the properties of a large electrical storage capacity and a high potential, is recognized as a very suitable material for the anode in cathodic protection installations. In this paper details are given of an alloy containing about 90% of magnesium which is more suitable for the anode than commercial magnesium, as well as of a bentonite-gypsum mixture for use as the electrolyte which is packed round the anode.

Laboratory Studies for Determination of Organic Acids as Related to Internal Corrosion of High Pressure Condensate Wells. E. C. Greco and H. T. Griffin. (Corrosion, 1946, vol. 2, Sept., pp. 138-152). Severe internal corrosion of high-pressure gas-condensate oil-well tubing and fittings has been the subject of investigations in the Mexican Gulf oil industry. The corrosion was at first attributed to carbon dioxide in the gas, but it was later found that organic acids form an important contributing factor to the severe corrosion. In this paper methods of isolating and determining the concentration of organic acids in condensate water are described.

Designing Water Pipes for Long Life and High Carrying Capacity. G. H. Garrett. (Corrosion, 1946, vol. 2, Sept., pp. 154-162). Corrosion studies of a number of large-diameter steel pipe lines for water supplies in the United States are described. Experience proves that buried lines coated externally with coal-tar enamel will have a long life.

Corrosion of Underground Structures in Gas Plants. C. F. Mayerherm and A. F. Ganz. (American Gas Association: Gas World, 1946, vol. 125, Aug. 31, pp. 236-238). The causes of the corrosion of underground structures at gasworks are discussed with special reference to the origin of stray currents and means of eliminating them.

Changes in Metallic Surfaces Due to Flowing Water. M. Vater. (Zeitschrift für Metallkunde, 1944, vol. 36, Feb., pp. 38-43). In order to study cavitation effects, a rectangular tube 170 mm. long with a section 30×10 mm. was built into a 50-mm. dia. pipeline through which water was pumped at 40 m./sec. The turbulent flow produced temper colours on the walls of this cavitation chamber. Marked colouring occurred in both carbon and low-alloy steels, whilst there was less colour effect on Silumin and no colours at all on stainless steel and copper-aluminium-silicon bronze. These colours are caused by the oxide film which forms on the surface of the metal. The question whether local temperature peaks can arise from the impact of drops of liquid has not yet been answered, but there is evidence that these (theoretically possible) peaks have, in practice, no effect on the behaviour of metals subjected to impacts by water.

Manual of Operation for Salt Spray Testing Equipment. H. P. Troendly. (Monthly Review of the American Electroplaters' Society, 1945, vol. 32, Nov., pp. 1110-1114). In 1944, A.S.T.M. Specification B117-44T on a salt-spray testing cabinet was revised. In this paper full details of the operation of

this testing apparatus, which enable reproducible results to be obtained, are given.

The Reaction of Lead Compounds. J. E. O. Mayne. (Journal of the Society of Chemical Industry, 1946, vol. 65, July, pp. 196-204). It has been shown that distilled water may be rendered non-corrosive by contact with lead powder, litharge, and red lead, whilst under the same conditions little or no inhibition was obtained from lead peroxide, lead sulphate, lead chromate, basic lead sulphate, basic lead carbonate, iron oxide, and titanium oxide. The inhibition was associated with the passage of lead into solution. Atmospheric carbon dioxide removed the lead from solution by precipitating it as basic lead carbonate. In certain cases, therefore, protection broke down, and the results were not very reproducible. Paints have been prepared with the majority of the pigments mentioned above, by grinding them in a drying oil, and it has been found that, so long as the lead pigment was sufficiently basic to form lead soaps, it yielded a paint film which was capable of making water non-corrosive. It was concluded, that inhibition was brought about by the soluble lead compounds produced by the hydrolysis of lead soaps, and this was confirmed by an examination of the behaviour of a commercial sample of lead linoleate. This inhibition was obtained even in the presence of small quantities of electrolytes and atmospheric carbon dioxide. It would seem that the ideal vehicle should contain sufficient acid to ensure adequate soap formation, and should yield a film of maximum water resistance, in order that the soluble inhibitive ingredients may be retained as long as possible. The possible ways in which such a vehicle could be developed are discussed in the paper. The mechanism by which the products of hydrolysis of lead linoleate cause inhibition has been examined, and it is concluded that the soluble lead compounds are adsorbed on the bare metal, and act as anodic adsorption inhibitors. The nature of the adsorbed substance has not been clearly established. The paper contains suggestions for future work.

Water Immersion Testing of Metal Protective Paints. W. W. Kittelberger and A. C. Elm. (Industrial and Engineering Chemistry, Industrial Edition, 1946, vol. 38, July, pp. 695-699). A paint system consisting of one coat of zinc-chromate primer and one coat of low-gloss, alkyd hull paint was applied to panels of iron, aluminium, zinc, and glass, and immersed for periods of up to 35 days in distilled water, sodium chloride, and sugar solutions with osmotic pressures of 6-30 atm. The rates and degrees of water absorption and blistering were determined by extensive measurements of weight and volume changes. Regardless of the nature of the solution and the plate material, the absorption of water and blistering increased with increasing immersion time, but decreased markedly with increasing osmotic pressure of the bath. The evidence obtained proved that the water is transferred through the face of the paint under the influence of, and at a rate determined by, the difference in osmotic pressure of the bath solution and of the solution formed within the paint system by the water absorbed. If the osmotic

pressure of the external solution is high enough, blistering does not take place. The minimum osmotic pressure of the external solution necessary to prevent blistering varies with the nature of the material painted.

The Influence of Movement on the Corrosion of Metals in Salt Solutions and Natural Waters. Part I. Low-Speed Rotation of Mild Steel: Peripheral Velocities below 100 Ft./Min. F. Wormwell. (Iron and Steel Institute, 1947, this Journal, Section I.). A rotating-specimen technique, using 1-in. dia. cylinders of mild steel at speeds up to 260 r.p.m., has been devised for investigating the influence of movement on the corrosion rates of immersed metals. Measurements of oxygen absorption, hydrogen evolution, loss of weight of metal, and depth of penetration of corrosion into the metal have been made with mild steel in 0.5*N* sodium chloride, "conductivity" water, a hard supply-water, and sea-water. Evolution of hydrogen gas corresponds with a negligibly small proportion of the total corrosion of mild steel, except in sea-water, where it comprises about 5% at 43.3 r.p.m.

Corrosion-time curves for 0.5*N* sodium chloride are made up of linear branches, but those for conductivity water, hard supply-water, and sea-water are more complex. The maximum rate of penetration in 0.5*N* sodium chloride at 260 r.p.m. is about 7 mm./year. In 0.5*N* sodium chloride the corrosion rate at 2 r.p.m. is three times, and that at 260 r.p.m. only twelve

times, the rate in a stagnant solution. A tentative explanation is advanced. Factors influencing the distribution of corrosion are discussed, and it is concluded that the positions of anodic and cathodic areas cannot always be located precisely. The corrosion process is, however, considered to be essentially electrochemical.

The Protection of Iron and Steel by Metallic Coatings. Results of Five Years' Exposure Tests. J. C. Hudson and T. A. Banfield. (Iron and Steel Institute, 1947, this Journal, Section I.). An account is given of the observations made to date on the behaviour of a wide range of protective coatings applied to mild steel exposed to field corrosion tests as part of the investigations of the Protective Coatings (Corrosion) Sub-Committee. These results cover periods of up to five years in the case of atmospheric exposure and of two years in that of immersion in sea-water. The coatings under investigation are aluminium, cadmium, lead, tin, and zinc, together with 82/18 cadmium-zinc alloy and 88/12 lead-tin alloy ("terne"). These were applied in one or more of three standard thicknesses, nominally 1, 3, and 5 mils., by a wide variety of processes, including cementation, electro-deposition, hot-dipping, and spraying. In the last case, specimens were prepared by three types of metal-spraying process, namely, the molten-metal pistol, the powder pistol, and the wire pistol. A summary of the results will be found in the text.

ANALYSIS

(Continued from p. 101 A)

The History and Present Status of Emission Spectroscopy as Applied to Industry. J. Convey. (Metallurgia, 1946, vol. 34, Oct., pp. 331-335). The history of emission spectroscopy is traced from its beginnings in the discoveries of Galileo up to the present day.

High Speed Spectrography. L. E. Owen. (Iron Age, 1946, vol. 158, Aug. 8, pp. 50-53; Aug. 15, pp. 61-64). Details are given of modifications to spectrographic equipment which increased the number of determinations which could be made in a given time, and facilitated operation by unskilled labour. The spectrograph and the major components of the spark source were enclosed in a safety hood, several manual controls were eliminated, a motor drive was fitted to the plate carriage of the densitometer, and solenoid operation was fitted to the slit head assembly. The rotary calculator for converting the density of the recorded spectra to the concentration of the alloying elements present is described.

The Spectrochemical Analysis of Steels with a Direct-Reading Instrument. M. F. Hasler, J. W. Kemp, and H. W. Dietert. (A.S.T.M. Bulletin, 1946, Mar., pp. 22-25). A description is given of a direct-reading spectrographic apparatus consisting of a special spectrometer containing up to twelve receivers, a recording console which has a recorder for each receiver, and a source unit providing the means for exciting a high-intensity spectrum of the sample to be analyzed under a variety of excitation conditions.

Some Modern Aids to Spectrochemical Analysis. B. S. Cooper. (Analyst, 1946, vol. 71, Aug., pp. 356-361). Attention is drawn to special devices which have enabled emission and absorption spectroscopy to attain their full status as reliable quantitative procedures. These include developments in connection with light sources and energy receivers.

Light Integrating Exposure Switch for Spectrographic Analysis. H. R. Clayton. (Journal of Scientific Instruments, 1946, vol. 23, Oct., pp. 233-234). A description is given of an automatic exposing device for obtaining spectrograms of consistent density and the exclusion of personal errors from spectrography. A fixed pre-sparking period is followed by an exposure during which the light emitted by the source is measured. When the amount of light emitted reaches a predetermined value, the source is extinguished.

The Determination of Low Aluminium Contents in Steel by Spectrum Analysis. C. G. Carlsson. (Iron and Steel Institute, 1946, Translation Series, No. 290). This is an English translation of a paper which was published in *Jernkontorets Annaler*, 1942, vol. 126, No. 5, pp. 161-176. (See *Journ. I. and S.I.*, 1943, No. 1, p. 145 A).

The Determination of Small Amounts of Aluminium in Steel. F. W. Box. (Armaments Research Department, Woolwich: Analyst, 1946, vol. 71, July, pp. 317-319). In this method of determining small

amounts of aluminium in steel the aluminium is precipitated as hydroxide along with the hydroxides of chromium, titanium and zirconium (if present), and some iron, from a solution of the steel in dilute sulphuric acid, by the cautious addition of ammonia or a weak organic base. Finally the iron can be converted into a complex cyanide from which the aluminium can be precipitated with 8-hydroxyquinoline. Titanium and zirconium are also precipitated and must be removed with cupferron.

Spectrographic Determinations of Small Aluminium Contents in Ordinary and Special Steels. R. Castro. (Metal Treatment, 1946, vol. 13, Autumn Issue, pp. 182-196). The development of a spectrographic method of determining aluminium in steel of relatively low alumina content is described. Cylindrical steel specimens 3.5 mm. in dia. are used as electrodes and these are sparked. The mean absolute error is $\pm 0.0006\%$ for contents between 0.004% and 0.025%. A method of determining the dissolved aluminium, using hydrochloric acid solutions with a low iron content, is also proposed.

Fluorometric Determinations of Aluminium in Steels, Bronzes, and Minerals. A. Weissler and C. E. White. (Industrial and Engineering Chemistry, Analytical Edition, 1946, vol. 18, Sept. 21, pp. 530-534). A rapid fluorometric method is described for the determination of aluminium in the range 0.001-1% in steels, bronzes, and minerals. The use of a micro-technique is avoided by taking aliquot parts of a macro-sample. For small percentages of aluminium the method is superior to others in respect of speed, sensitivity (1 part in 100,000,000), accuracy, and freedom from interference. The reagent preferred is Pontachrome Blue Black R, in a buffered solution of pH 4.8, or as an alternative Pontachrome Violet SW. Interfering ions are eliminated by electrolysis in a mercury cathode cell. The influences of changes in intensity in fluorescence caused by variations in temperature, time, pH value, dye concentration, and aluminium concentration have been studied.

Spectrographic Determination of Boron in Steel. C. H. Corliss and B. F. Scribner. (Journal of Research of the National Bureau of Standards, 1946, vol. 36, Apr., pp. 351-364). The spectrographic determination of small amounts of boron in thin

steel rods and in massive pieces of steel was investigated by using several types of arc-like discharges. The sensitivity and accuracy in determining boron were found to be affected by variations in the rate of cooling of the electrodes. With $\frac{3}{32}$ -in.-dia. electrodes and a high-voltage A.-C. arc, amounts down to 0.0006% of boron could be determined, with an average deviation of $\pm 4\%$; with more massive specimens this arc is insensitive, but an overdamped condenser discharge or similar source provides adequate sensitivity and precision. Amounts as low as 0.0001% of boron can be determined with a D.C. arc to which sodium is added to suppress the iron spark line Fe II 2497.82 Å.

The Determination of FeO in Steel from the Rate of Carbon Drop. R. J. Sarjant. (Iron and Steel Institute, 1947, this Journal, Section I.). The paper gives several forms of nomographs applicable to the determinations of FeO in molten steel from the carbon drop. The original basis was developed by Schenck, Riess, and Brüggeman. A variation of equilibrium temperature is included in a revised nomograph, calculated from the free-energy equations of Vacher and Hamilton. Some correlation was found with results of oxygen determinations reported by Bramley, Maddocks, and Tateson. A simpler nomograph was also constructed for use at 1600°C.

A review of the previous work on the determination of FeO in molten steel, and on the values of the velocity and equilibrium constants required for an accurate definition of the fundamental equation governing the reaction between FeO and carbon, reveals the controversial nature of the subject and the need for further experimental enquiry to establish the accuracy of the data.

The Rapid Determination of Reactive Oxygen in Open-Hearth Steel. I. M. Mackenzie. (Iron and Steel Institute, 1947, this Journal, Section I.). An experimental method of determining the reactive oxygen in liquid steel is described. The results so obtained are shown to correlate with the carbon content and the rate of carbon drop. A formula expressing the relationship is derived enabling the reactive oxygen, during the later stages of the boil, to be calculated or determined graphically from the carbon-drop curve.

BOOK NOTICES

(Continued from pp. 101 A-103 A)

AMERICAN FOUNDRYMEN'S ASSOCIATION. "*Handbook of Cupola Operation.*" 8vo, pp. xxi + 470. Illustrated. Chicago, 1946: The Association. (Price 28s. 6d.)

This is a complete and authoritative reference book dealing exclusively with the operation of the cupola. Its contents cover cupola construction, lining, charging equipment, blowing equipment, blast control, fuel, slags and fluxes, thermal equilibrium, and the actual details of successful operation. It includes a complete bibliography of about 500 references.

DUBOIS, J. H., and W. I. PRIBBLE. "*Plastics Mold Engineering. The Fundamentals of Plastics Mold Design and Construction.*" 8vo, pp. ix + 494. Illustrated. Chicago, 1946: American Technical Society, London: The Technical Press, Ltd. (Price 45s.)

This book describes the design of the important types of moulds and indicates their use. Constructional methods commonly employed are explained and certain chapters deal with individual types of moulds and specific moulding processes. A short chapter describes the various raw

materials used for mould parts and another deals with the maintenance and repair of moulds.

GIFFEN, EDMUND. "*Engineering Research in the Universities.*" 8vo, pp. 12. London, 1946: Oxford University Press. (Price 1s. 6d.)

Professor Giffen, in an inaugural lecture to the Chair of Civil and Mechanical Engineering at the London University, deploras the relative lack of co-operation between Universities and Industry in Engineering Research.

Whilst appreciating the fact that Universities must necessarily confine themselves to the more fundamental aspects of research, he points out that, for this to be of maximum value, it must be closely related to the applied research normally carried out by industrial firms and associations.

He further draws attention to the fact that industry relies very largely on the Universities for the production of the skilled man-power qualified to carry out research work, and suggests that Research Associations would be well advised to make more use of existing research facilities at Universities by proposing specific problems, and, where necessary, making a contribution towards the cost of the work. This might also have the advantage of attracting young research workers at the Universities, after the completion of their normal courses, to industrial engineering laboratories.

HARWOOD, P. B. "*Control of Electric Motors.*" Second Ed. 8vo, pp. vii + 479. Illustrated. New York, 1944: John Wiley and Sons, Inc.: Chapman and Hall, Ltd. (Price, 33s.)

The first edition of this book made its appearance in 1936. In this new edition a complete chapter on synchronous motor control and variable-voltage control has been added, and many new tables giving the ratings of motors and controllers have been included.

LEA, F. C., and E. N. SIMONS. "*The Machining of Steel Simply Explained.*" 8vo, pp. vi + 214. Illustrated. London and Glasgow, 1945: Blackie and Son, Ltd. (Price 8s. 6d.)

In this little handbook the authors present the fundamental principles of the machining of steel as clearly and as simply as possible. Their aim has been to help every operator—skilled, semi-skilled or unskilled—to secure better results from the machines in his care and the tools he uses. Throughout, the emphasis has been on lucidity. Every sentence was written and every chapter planned, with a view to being fully understood. Part I. deals with the machines; Part II. with the principles; Part III. with the tools and Part IV. with operations.

PIRENNE, M. H. "*The Diffraction of X-Rays and Electrons by Free Molecules.*" 8vo, pp. xii + 160. Illustrated. Cambridge, 1946: University Press. (Price 12s. 6d.)

Professor Debye writes, in his Foreword of this book: "It contains all essential information about a subject intimately connected with modern advances of our understanding of molecular structure. The theoretical development is logically followed through from its beginning to the very end, without insisting on mathematical details, but always leading to the point where the actual magnitude of the effect is evaluated. Nowhere is the experimental evidence neglected or the practical side treated superficially, and at every occasion the theory is put to the test by confrontation."

PIWOWARSKY, E. "*Hochwertiges Gusseisen, seine Eigenschaften und die physikalische Metallurgie seiner Herstellung.*" 8vo, pp. ix + 1005. Illustrated. Berlin, 1942: Springer-Verlag. (Price £7 7s.)

This book contains the following chapters: I. Einleitung; II. Allgemeine konstitutionelle Grundlagen; III. Die konstitutionellen Grundlagen der Eisen-Kohlenstofflegierungen; IV. Über den molekularen Aufbau kohlenstoffhaltiger Lösungen; V. Der Einfluss des Siliziums auf die Gleichgewichts- und Graphitisierungsvorgänge; VI. Der Mechanismus der Graphitbildung siliziumhaltigen Eisens; VII. Die strukturelle Beherrschung der metallischen Grundlagen; VIII. Die Primärkristallisation des Gusseisens; IX. Der Einfluss der ständigen Eisenbegleiter; X. Der Einfluss der Gase; XI. Wärmetönungen metallischer Reaktionen; XII. Technologische Eigenschaften flüssiger und erstarrender Eisen-Kohlenstofflegierungen; XIII. Technologische Eigenschaften des festen Gusseisens; XIV. Die mechanischen und elastischen Eigenschaften des Gusseisens; XV. Die physikalischen Eigenschaften; XVI. Die Eigenschaften bei höheren und tieferen Temperaturen; XVII. Die chemischen Eigenschaften des Gusseisens; XVIII. Der zusätzliche Oberflächenschutz von Gusseisen; XIX. Der Einfluss der Korrosion auf die Festigkeitseigenschaften; XX. Der Einfluss thermischer Nachbehandlung auf die Gefügeänderungen und die Eigenschaften perlitischer Grundmassen; XXI. Legiertes Gusseisen; XXII. Die Kalt- und Warmverformung des Gusseisens; XXIII. Das Schweißen von Gusseisen; XXIV. Fehlerquellen bei der Gefügeuntersuchung von Gusseisen; XXV. Das Schmelzen von Gusseisen im Kupolofen; XXVI. Andere Schmelzöfen; XXVII. Gusseisen für einige spezielle Verwendungszwecke.

SAWYER, R. T. "*The Modern Gas Turbine.*" 8vo, pp. xx + 216. Illustrated. London, 1945: Sir Isaac Pitman & Sons, Ltd. (Price 21s.)

This book contains the following chapters: Fundamentals; Early Inventions and History of the Gas Turbine; The Gas Turbine Using Diesel Engine Exhaust Gases, as a Supercharger or as a Prime Mover; Combustion Gas Turbine Calculations and Efficiencies; The Gas Turbine in Industry; The Gas Turbine in Marine Service; The Gas Turbine Locomotive; The Exhaust Turbo-Supercharger on Aircraft Engines; The Gas Turbine as an Aircraft Prime Mover, Including Jet Propulsion.

TIMOSHENKO, S., and D. H. YOUNG. "*Theory of Structures.*" 8vo, pp. xiv + 488. Illustrated. New York and London, 1945: McGraw-Hill Book Co., Inc. (Price 25s.)

In the preparation of this book, the authors have tried to keep in mind the fact that the theory of structures is based on mechanics with which the student is already familiar. Thus by establishing a close relationship between the teaching of mechanics and structures, the book helps the student to understand the various practical methods of analysis of trusses and frames. With this point of view, the first chapter offers an introduction to the theory of structures in which the basic principles of statics are recapitulated. Succeeding chapters deal with the analysis of statically determinate trusses in one plane, influence lines, formation and analysis of space trusses with hinged joints, principles of mechanics preparatory to the analysis of statically indeterminate structures, methods of calculating deflections of trusses, theory of statically indeterminate trusses, bending of beams and frames, and the theory of arches.

TIRANTI, D., with the collaboration of W. F. WALKER. "*Introduction to Production Control.*" 8vo, pp. xix + 159. Illustrated. London, 1946: Chapman and Hall, Ltd. (Price 15s.)

This book, which explains the whole method and working of a production control system, is intended as an introduction to the subject and includes many charts and diagrams which help to make clear the details involved.

SUBJECT INDEX.

[References to the papers read before the Institute are indicated by the word *Paper* following the page number. The letter *P.* denotes a reference in Section I. of the Journal which contains the reports of the proceedings of meetings, the papers read, and the discussions thereon. The letter *A.* denotes a reference to the section dealing with abstracts.

Indexing of Alloy Steels and Other Alloys. In the indexing of alloy steels, carbon and iron are ignored and the alloying elements contained in the steel are arranged in alphabetical order; for example all references to nickel-chromium-molybdenum steel will be found under the heading chromium-molybdenum-nickel steel. In the indexing of other alloys, carbon and iron, when present, are included in the title; iron, when present, is always mentioned first and the other elements follow in alphabetical order, carbon being in all cases mentioned last. Examples: "Iron-silicon-carbon alloys" and "iron-chromium-nickel-carbon alloys."]

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